positive particles than negative ones. In a very short time, less than two minutes, only negative particles remained suspended. The positive particles, which could be seen to settle out very rapidly, apparently had all settled out and left only negatively charged particles. Kruyt and DeKadt[12] reported that charcoal activated at 1000° gave positively charged particles, while charcoal activated at 400° gave negatively charged particles. Kolthoff[4] observed the same relation between particle charge and temperature of activation. Frampton and Gortner[13] attempted to prepare positively charged charcoal but did not succeed in doing so; they reported only negatively charged particles for charcoal activated at 1000°. Wiegand[14] reported that lampblack which was collected by being attracted to a negative plate and, therefore, must have had a positive charge, proved to have a negative charge in an aqueous suspension. Further research regarding the charge of "High Temperature Charcoal" will probably clear up this apparent contradiction in the results on the particle charge for such charcoal.

A summary of the data obtained for all the charcoals is given in Table IV.

Summary

1. Preferential adsorption from benzene–ethanol solutions by charcoals activated at different temperatures and in different gases shows that charcoal can be changed from extremely organophilic charcoal to charcoal approaching in adsorptive properties the hydrophilic adsorbent, silica.

2. The characteristic S-shaped preferential adsorption curves for a series of increasingly hydrophilic charcoals have been plotted, and the points where these curves cross the X-axis, the X_0 values, are shown to be a measure of the relative organophilic or hydrophilic nature of the charcoals.

3. The organophilic "high temperature charcoal" (activated at temperatures near 1000°), when suspended in water, gave both positively and negatively charged particles. This charcoal gave acid adsorption but no base adsorption. The less organophilic "medium temperature charcoal" (activated at temperatures near 400°), when suspended in water, gave only negatively charged particles. This charcoal gave base adsorption. The "low temperature charcoal" (activated in a highly oxidizing atmosphere below 150°), approaching in adsorptive properties hydrophilic silica, when suspended in water, gave only negative particles. This charcoal showed both acid and base adsorption.

ANN ARBOR, MICHIGAN RECEIVED MARCH 17, 1938

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[12] H. R. Kruyt and G. S. DeKadt, *Kolloidchem. Beihefte*, **32**, 349 (1931).

[13] V. L. Frampton and R. A. Gortner, *J. Phys. Chem.*, **41**, 567 (1937).

[14] W. B. Wiegand, *Ind. Eng. Chem.*, **29**, 953 (1937).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF BRITISH COLUMBIA]

Physical Chemical Properties of *cis-* and *trans-*Decahydronaphthalene[1]

BY W. F. SEYER AND R. D. WALKER

Introduction.—Little is known of the chemical and physical properties of the dicyclic naphthalene hydrocarbons. An extensive investigation of these compounds can be undertaken only after a method has been found for obtaining these two compounds in a high state of purity and in suitable quantities. The wide variation in the physical data of the two isomeric forms as given by Hückel[2] in his summary of the literature dealing with this subject would indicate that in some of the methods of synthesis the two forms were produced simultaneously, but in varying amounts.

It was thought, therefore, that the most practical method of obtaining the two forms in sufficient quantity was to fractionate the commercial decalin.

Fractionating Apparatus.—It was discovered in a series of preliminary trials that reduced pressure must be used. Decomposition took place during distillation at atmospheric pressure even with a column length of only 1 meter. The complete apparatus used is shown in Fig. 1. The diagram is self-explanatory; hence only a few remarks are necessary to describe the mode of operation. By utilizing a magnet controlled receiving unit, stopcocks at this point were eliminated. The reflux was controlled by sealing a fine capillary tube to the head of the rectifying column. The lagged column was packed with No. 18 galvanized jack chain. The still had a capacity of 3000 cc. and was electrically heated. Water at 20° was pumped from a constant temperature bath to the condensers.

The reduced pressure of 10 mm. was maintained by a Cenco vacuum pump. At this pressure it was found that no pressure regulation device was required to keep the height of mercury in the manometer constant. A sulfuric acid manometer in connection with the one above showed variations in pressure of less than 1 mm.

Materials.—Decalin from various sources was used. Material from the Eastman Kodak Co. showed a consider-

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[1] Original manuscript received August 20, 1937.

[2] Hückel, *Ann.*, **441**, 1 (1925).

able variation as judged by the density and refractive index. All samples showed some coloration when shaken with concentrated sulfuric acid. However, irrespective of whether or not the decalin had been treated with acid until no further coloration took place, the freezing points of the ultimate products were all the same within the limits of experimental error.

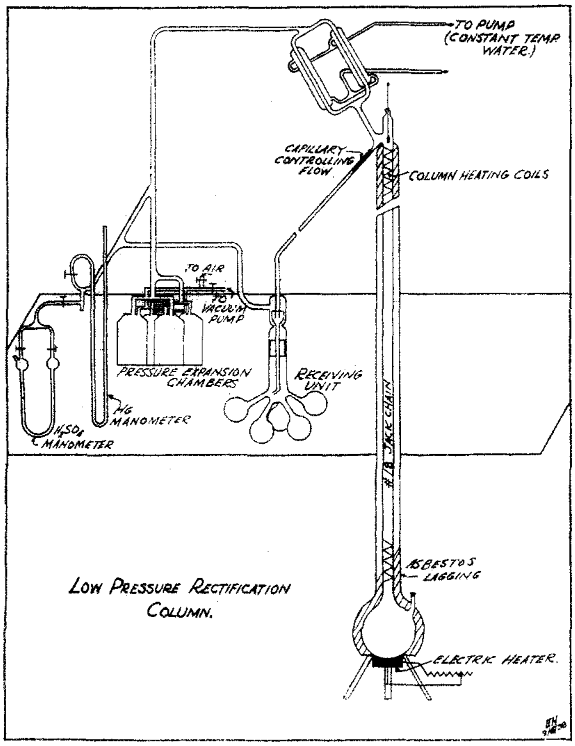

Fig. 1.

Methods of Purification and Procedure.—Two fractional distillations were carried out on each sample of decalin, followed by fractional crystallization until a constant freezing point was obtained. A summary of a typical distillation run is given below.

Table I

Charge, 2065 cc. of decalin about 45% *cis*. Distillation pressure 10 mm. Condenser water at 20°.

Fractions	1	2	3	4	5
Vol., cc.	205	440	483	460	310
Temp. at top of column, °C.	41.0–62.2	62.2–63.7	63.7–67.4	67.4–69.2	69.2–69.9
Time, hrs.	1.67	3.50	4.33	4.83	3.33
Rate, cc./hr.	123	126	112	95	93
$n^{20}D$	1.47050	1.47093	1.47404	1.47892	1.48082
Total time	17.66 hrs.		Total distillate		1900 cc.
Residue	120 cc.		Loss		45 cc.

Fractions 1 and 2 of this and other runs were then added together and again distilled. Nos. 4 and 5 were treated in a similar manner. The first lot upon the second distillation yielded a fraction of a little over 500 cc. with b. p. 60.3 to 62.7° and refractive index, $n^{20}D$ 1.46967, corresponding to the value given by Hückel for the *trans* form. A fraction totaling 425 cc. with b. p. 69.5 to 69.7° was selected as the pure *cis* form. The refractive index $n^{20}D$ was 1.48116 as compared with Hückel's value of 1.48054.

Freezing Point Determination.—The freezing point of the selected fractions was next determined with two Leeds and Northrup quartz encased potential terminal, platinum resistance thermometers of the following characteristics.

	R at ice point	*F*	δ
Thermometer I	2.5461	0.9941	1.504
Thermometer II	2.5117	.9732	1.502

Thermometer I has shown a change of only 0.0001 ohm in the ice-point over a period of ten years. Thermometer II, on the other hand, had shown a drift, and had therefore been sent to the Bureau of Standards for recalibration shortly before.

The freezing point apparatus consisted of two Dewar tubes. The outer one had a capacity of about 4 liters and was filled with dry ice. The inner tube, having a diameter of about 7 cm. and a depth of 20 cm., had attached to it a stopcock, such that the air pressure inside could be regulated at will, thereby giving any desired rate of cooling.

The change in the freezing point curves with progressive purification is shown in Figs. 2–4.

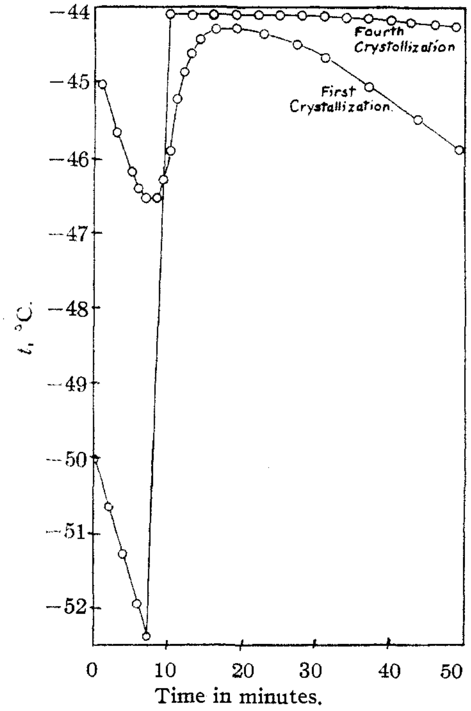

Fig. 2.—Cooling curves (*cis*).

If the slope of the freezing point curve is taken as a criterion of purity, the final (Fig. 4) curves of both the *cis* and the *trans* forms indicate a high state of purity. The final freezing point represents the ninth recrystallization and was taken only after the samples had been in contact with sodium wire for about ten days.

Inasmuch as the liquids were rather viscous at the freezing point it became of interest to find out just how accurately this point could be determined. Hence freezing point

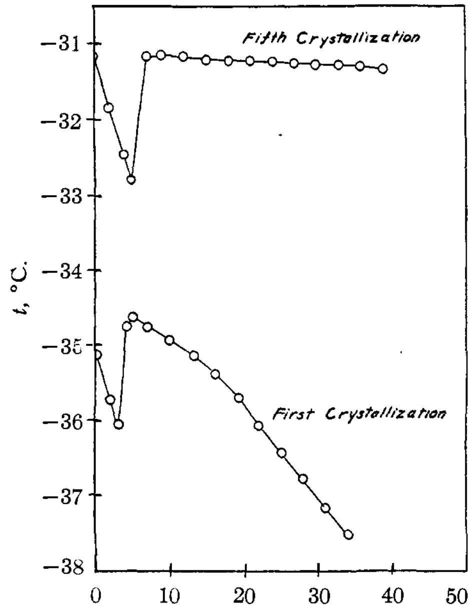

Fig. 3.—Cooling curves (*trans*).

determinations were made first with one thermometer and then with the other, next with constant rotary stirring by means of a propeller driven by a motor, then reciprocatory stirring by hand, and finally no stirring at all during the freezing period. The liquid was seeded with crystals in all cases. The results for the *cis* form were, respectively, −43.25, −43.26, −43.29, −43.23, −43.26°, with a deviation from the mean of 0.03°. The freezing point of the *cis* form is therefore given as −43.26 ± 0.04° and that of the *trans* form as 31.48 ± 0.04°. The last is an average of three determinations, −31.47, −31.46, −31.50°.

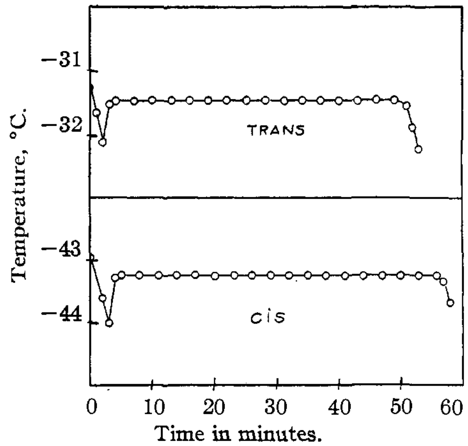

Fig. 4.—Final freezing point curves.

Boiling Point Determinations.—The method outlined in "Laboratory Methods of Organic Chemistry" by Gatterman (Macmillan) was followed closely. The thermometer used was one from an Anschütz set and was calibrated against one of the platinum resistance thermometers used in the previous determination. The boiling points corrected to 760 mm. were as follows; *cis*, 194.6°; *trans*, 185.5°.

Refractive Index.—The refractive indices were measured by a Hilger Pulfrich refractometer. Here two calibrated glass thermometers, graduated in tenths, were used. The one was in a constant temperature bath and the other in the refractometer itself.

Densities.—The densities of the pure compounds as well as the mixtures were measured by means of a modified Perkin pycnometer and are the average of three separate determinations.

Nine solutions of the two isomers were prepared by weight. The densities and refractive indices for D, C, G lines of these solutions were next measured. The results are given in Table II.

TABLE II

Concn. by wt. % *trans.*	d^{20}_4	n^{20}D	n^{20}C	n^{20}G′
0	0.8963	1.48113	1.47869	1.49881
10.05	.8934	1.47991	1.47742	1.49762
19.66	.8910	1.47890	1.47632	1.49661
29.69	.8885	1.47770	1.47526	1.49533
39.41	.8858	1.47667	1.47413	1.49429
49.88	.8832	1.47550	1.47292	1.49318
59.84	.8808	1.47437	1.47188	1.49205
69.72	.8779	1.47323	1.47069	1.49098
79.85	.8752	1.47206	1.46956	1.48960
89.77	.8725	1.47092	1.46854	1.48854
100	.8699	1.46968	1.46720	1.48727

Upon examining the properties of these mixtures of known composition, it was found that both density and refractive index were linear functions of the concentrations (Figs. 5, 6). The relationship between the per cent. *trans* form and the density is given by the equation $C = 3395 - 3788d$ when C is per cent. *trans* form and d is the

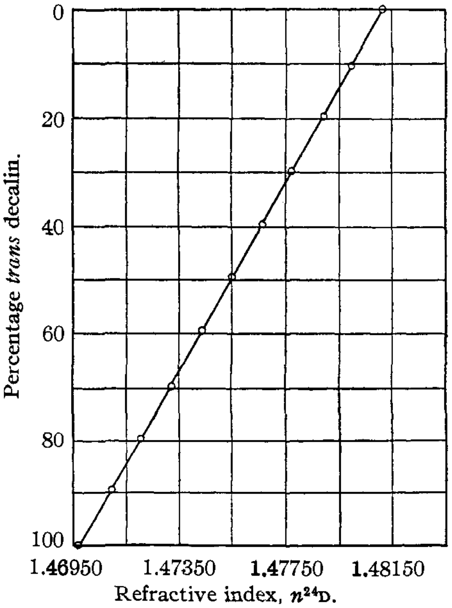

Fig. 5.

density at 20°, also $C = 12936 - 8734n$ when C is the same as above but n is the refractive index for the D line at 20°.

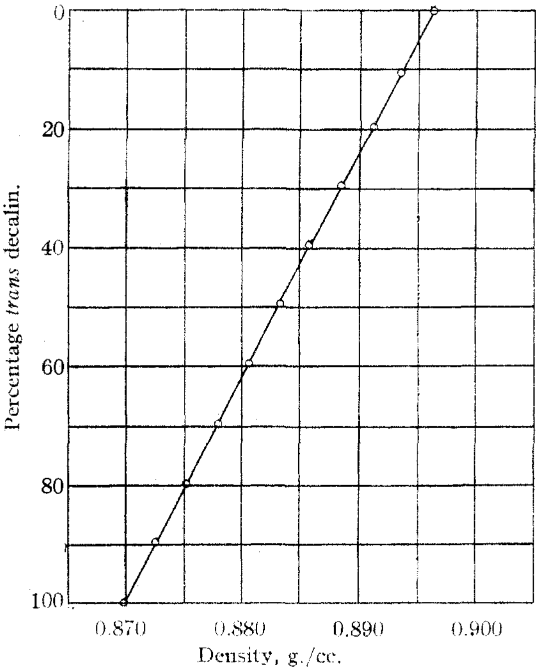

Fig. 6.

Attempts were made to determine the freezing points of the various mixtures by placing them in partially filled bulbs of about 20 cc. capacity. Because of the great amount of supercooling necessary and the low heat conduction of the hydrocarbons the results were only of qualitative significance. They indicated that the eutectic temperature lies between −60 and −70°.

A summary of the physical constants of the *cis* and *trans* forms of decahydronaphthalene is given in the following table.

TABLE III

	d^{20}_4	n^{20}_D	F. p., °C.	B. p. (760 mm.), °C.
cis form	0.8963	1.48113	− 43.26 ± 0.04	194.6
"Int. Crit. Tables"	.898			
Hückel[2]	.8952		− 51	
trans form	.8699	1.46968	− 31.47 ± 0.04	185.5
"Int. Crit. Tables"	.872	1.4701	−125	
Hückel[2]	.8695	1.46958	− 36	

Summary

1. Pure forms of *cis* and *trans* decahydronaphthalene have been prepared and some of their physical properties measured.

2. The freezing points were found to be higher than those so far recorded.

3. The densities and refractive indices of nine mixtures of the two forms were measured and it was shown that both these properties were linear functions of the compositions.

VANCOUVER, B. C. RECEIVED MAY 18, 1938

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF YALE UNIVERSITY]

The Thermodynamics of Hydrochloric Acid in Dioxane-Water Mixtures from Electromotive Force Measurements. V. Properties of the 45% Dioxane Mixtures

BY HERBERT S. HARNED AND JOHN G. DONELSON

Measurements of the electromotive forces of the cells

$$H_2 \mid HCl\,(m),\ \text{dioxane}\,(X),\ H_2O\,(Y) \mid AgCl\text{-}Ag$$

in 45% dioxane-water mixtures and at acid concentrations varying from 0.003 to 0.1 *M* have been reported by Harned and Morrison.[1] These measurements have been extended so as to include concentrations from 0.003 to 3 *M*. From these results and the standard potential of the cell,[2] the activity coefficient, relative partial molal heat content and specific heat have been computed. Similar results have been obtained by Harned and Ehlers[3] in water and by us[4] in 20% dioxane-water mixtures which in conjunction with present results yield an accurate and very comprehensive study of the thermodynamics of this acid in media of dielectric constants of approximately 80, 60, and 40.

Experimental Results

No further changes in the technique described by Harned and Morrison[5,1] and modified in a few details by us[4] have been made. The present results were obtained with the same care and

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[1] Harned and Morrison, THIS JOURNAL, **58**, 1908 (1936).

[2] Harned, *ibid.*, **60**, 336 (1938).

[3] Harned and Ehlers, *ibid.*, **55**, 2179 (1933).

[4] Harned and Donelson, *ibid.*, **60**, 339 (1938).

[5] Harned and Morrison, *Am. J. Sci.*, **33**, 161 (1937).