tus and technique on cyclohexanol, 2-methylcyclohexanol and 3-methylcyclohexanol are being reported at this time.

The following heat capacity equation[1] was used for the three reactions.

$$\Delta C_p = 7.28 - 0.0118T$$

Values of ΔH_0 and I in the free energy equation

$$\Delta F = \Delta H_0 - 16.77T \log T + 0.0059T^2 + IT$$

calculated from the experimental results by the method of least squares are listed in Table I.

TABLE I

VALUES OF ΔH_0, I, ΔF_{298}, ΔH_{298}, ΔS_{298}

Alcohol	ΔH_0	I	ΔF_{298}	ΔH_{298}	ΔS_{298}
Cyclohexanol	13,588[a]	17.09	6840	15,233	28.16 ± 0.25
2-Methylcyclohexanol	13,465	17.05	6705	15,110	28.20 ± .15
3-Methylcyclohexanol	13,380	17.29	6691	15,025	27.97 ± .20

[a] ΔH_0 for cyclohexanol was calculated from Kistiakowsky's value for ΔH_{355} (Kistiakowsky, *et al.*, THIS JOURNAL, **61**, 1868 (1939)).

It is apparent that the substitution of a single methyl group ortho or meta to the hydroxyl has no appreciable effect on the thermochemistry of the dehydrogenation of cyclohexanols.

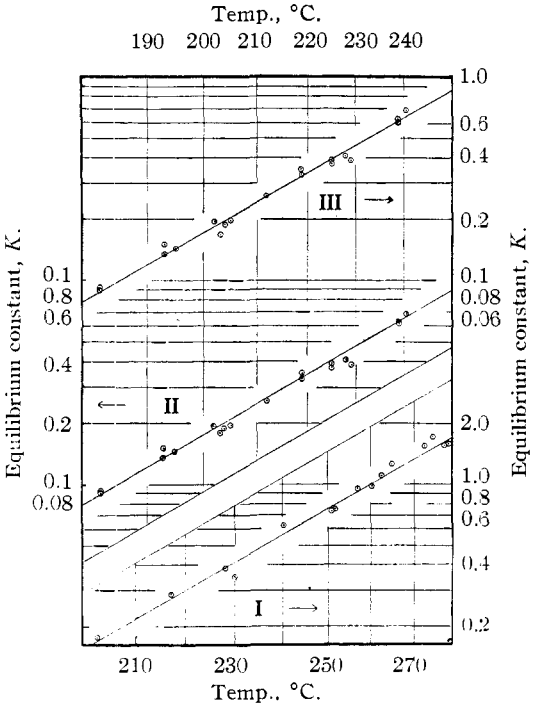

Fig. 1.—Log K *vs.* $1/T$ for dehydrogenation of: (I) cyclohexanol, (II) 2-methylcyclohexanol and (III) 3-methylcyclohexanol.

Experimentally determined values of the equilibrium constants are compared in Fig. 1, with the values calculated from the free energy equations.

RESEARCH LABORATORY
THE BARRETT DIVISION
ALLIED CHEMICAL & DYE CORPORATION
EDGEWATER, N. J. RECEIVED JANUARY 10, 1947

Numbers of Isomeric Alkylbenzenes

BY ALFRED W. FRANCIS

The exact numbers of structurally isomeric hydrocarbons of the paraffin series,[1,2] olefin series,[3] acetylene series,[4] and of their derivatives, alcohols, etc.[2,5] (or alkyl groups), and more complex derivatives[6] are listed in the literature up to 20 to 40 carbon atoms. Each series shows a progressive increase of about 2.5 fold for each additional carbon atom so that simple equations permit approximate extrapolation to any desired extent. It does not seem to have been noted that there are slight alternations in the ratio, which in the case of paraffin isomers is higher from odd to even number of carbon atoms than from even to odd, analogous to the increments of melting points of normal paraffin hydrocarbons as shown in Fig. 1; and that like the latter, the alternation gradually subsides with increasing carbon content, although it is still detectable at C_{40}.[7]

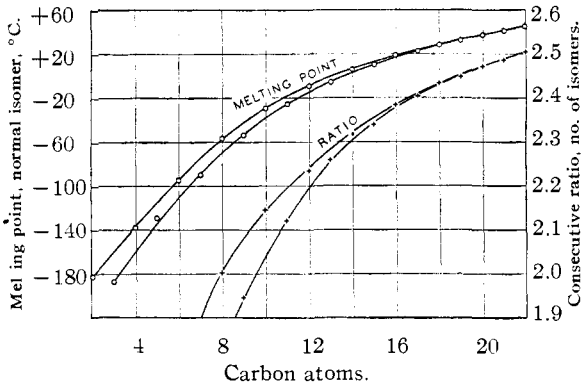

Fig. 1.—Analogy between alternations in melting points of normal paraffin hydrocarbons (physical observations) and in consecutive ratios in number of paraffin isomers (mathematical calculations).

The numbers of structurally isomeric alkylbenzenes are not listed beyond those with twelve carbon atoms[8] although mathematical equations are derived for the calculation of the number of isomers with any combination of substituents (one item in Table I).[8,9] In view of increasing

(1) Henze and Blair, THIS JOURNAL, **53**, 3084 (1931).
(2) Perry, *ibid.*, **54**, 2919 (1932).
(3) Henze and Blair, *ibid.*, **55**, 685 (1933).
(4) Coffman, Blair and Henze, *ibid.*, **55**, 253 (1933).
(5) Henze and Blair, *ibid.*, **53**, 3045 (1931).
(6) Henze and Blair, *ibid.*, **56**, 157 (1934).
(7) Logarithmic interpolation and allowance for the alternation mentioned permitted the detection of trifling errors in the listed numbers of paraffin isomers of 29 and 40 carbon atoms. The former was recalculated by the present author, giving the number, 1,590,507,821; and the latter was recalculated by one of the original authors (H. R. Henze, private communication) giving 62,481,806,147,341. Both numbers are consistent with the logarithmic interpolation, which is accurate to about half of the figures, provided neighboring numbers are correct.
(8) Polya, *Compt. rend.*, **201**, 1169 (1935); *Helv. Chim. Acta*, **19**, 23 (1936).
(9) T. L. Hill, *J. Phys. Chem.*, **47**, 253, 413 (1943); *J. Chem. Phys.*, **11**, 294 (1943).

TABLE I

No. substituents	1	2	3	4	5	6
All alike	1	3	3	3	1	1
All different	1	3	10	30	60	60
Two alike	..	3	6	16	30	30
Three alike	..	..	3	6	10	10
Two pairs	..	..	..	11	16	16
Four alike	..	..	..	3	3	3
Two alike and three alike	..	..	..	..	6	6
Five alike	..	..	..	..	1	1
Three alike and three alike	..	..	..	..	..	3
Two alike and four alike	..	..	..	..	..	3
Three pairs	..	..	..	..	..	11

importance of aromatic hydrocarbons, the exact numbers of these isomers are now computed up to a content of 24 carbon atoms.

The numbers of isomeric derivatives of benzene are shown in Table I (this applies to any substituents, *e. g.*, Cl, NO_2).

Using this table and the numbers of isomeric alkyl groups[5] (shown also in the top line in each column of Table II) the numbers of isomeric alkylbenzenes are calculated by itemizing the types and by summation as in Table II. Thus,

TABLE II

C_{10}		C_{12}		C_{13}		C_{14}	
Bu	4	Hex	17	Hept	39	Oct	89
MePr	6	MeAm	24	MeHex	51	MeHept	117
Et_2	3	EtBu	12	EtAm	24	EtHex[a]	51
Me_2Et	6	Me_2Bu	24	Me_2Am	48	Me_2Hex[a]	102
Me_4	3	Pr_2	9	PrBu	24	PrAm	48
	—	MeEtPr	20	MeEtBu	40	MeEtAm	80
	22	Me_3Pr	12	Me_3Bu	24	Me_3Am	48
		Et_3	3	$MePr_2$	22	Bu_2	30
		Me_2Et_2	11	Et_2Pr	12	MePrBu	80
		Me_4Et[a]	3	Me_2EtPr[a]	32	Et_2Bu[a]	24
C_{11}		Me_6	1	Me_4Pr[a]	6	Me_2EtBu	64
			—	$MeEt_3$[a]	6	Me_4Bu[a]	12
Am	8		136	Me_2Et_2	6	$EtPr_2$	22
MeBu	12			Me_3Et	1	Me_2Pr_2[a]	38
EtPr	6				—	$MeEt_2Pr$	32
Me_2Pr	12				335	Me_3EtPr[a]	20
$MeEt_2$	6					Me_5Pr[a]	2
Me_3Et	6					Et_4	3
Me_5	1					Me_2Et_3[a]	6
	—					Me_4Et_2[a]	3
	51						—
							871

[a] Not yet represented by known hydrocarbons.

for example, there are 80 methylpropylbutylbenzenes, obtained by multiplying 4 (kinds of butyl group), 2 (kinds of propyl group), and 10 from Table I. Types containing two or more alkyl groups of like carbon content above ethyl may be subdivided according to whether these groups are alike or unlike. Thus, for tributylbenzenes, there are 3 × 4 isomers with the three substituents alike, 6 × 4 × 3 isomers with two of them alike, and 10 × 4 isomers with all three different, a total of 124.

Table II has been extended similarly for alkylbenzenes containing 15 to 24 carbon atoms. The numbers increase a little more rapidly than in the case of the paraffin isomers[1,2] so that the ratio for the two series increases steadily as shown in Table III and should exceed 1.0 at C_{28}. Again there is an alternation in ratio of successive numbers, considerable at first, but quickly subsiding as shown in Fig. 2. Extrapolation would be still more precise using the ratio to number of alkyl groups,[2,5] which approaches 0.04718 asymptotically. This would give for C_{30} 4529 × 10^6.

TABLE III

Carbon atoms	Numbers of isomeric: Alkylbenzenes	Paraffins	Ratio
7	1	9	0.1111
8	4	18	.2222
9	8	35	.2286
10	22	75	.2933
11	51	159	.3208
12	136	355	.3831
13	335	802	.4177
14	871	1,858	.4688
15	2,217	4,347	.5100
16	5,749	10,359	.5550
17	14,837	24,894	.5960
18	38,636	60,523	.6384
19	100,622	148,284	.6786
20	263,381	366,319	.7190
21	690,709	910,726	.7584
22	1,817,544	2,278,658	.7976
23	4,793,449	5,731,580	.8363
24	12,675,741	14,490,245	.8748

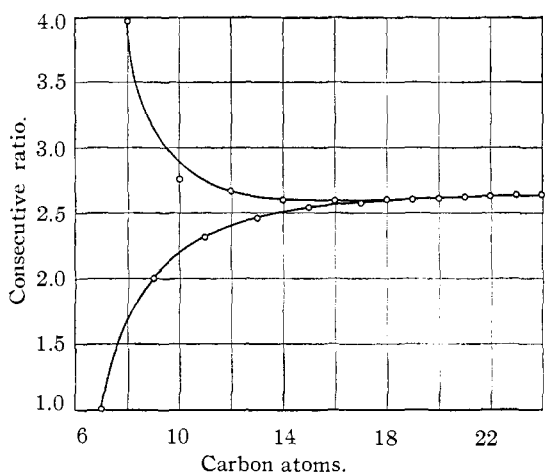

Fig. 2.—Alternations in consecutive ratios in number of isomeric alkylbenzenes.

SOCONY-VACUUM LABORATORIES
(DIVISION OF SOCONY-VACUUM OIL CO., INC.)
RESEARCH AND DEVELOPMENT DEPARTMENT
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Halogen–Metal Interconversions with Halides Containing Functional Groups

BY HENRY GILMAN AND CLYDE E. ARNTZEN[1]

In connection with studies concerned with physiological action, it was necessary to have

(1) Present address: Research Laboratories, Westinghouse Electric and Manufacturing Co., East Pittsburgh, Pa.