

NEW REGULARITIES IN THE PHYSICOCHEMICAL PROPERTIES OF HYDROCARBONS. II*

V. M. Tatevskii and V. A. Benderskii

In preceding papers [1-3] we have shown that a series of hydrocarbon properties (those properties which as a rule contain capacity factors, for example: molar volume V , molar refraction R , heat of formation from atoms $\Delta H_{(at.)}$ or elements $\Delta H_{(el.)}$, heat of combustion $\Delta H_{(comb.)}$, heat of vaporization L , logarithm of the vapor pressure $\log p$ et al.), when converted to molar units are a linear function of the number (n) of carbon atoms in the hydrocarbon molecule. According to the theoretical ideas previously developed by us [1, 3], this linearity should be observed for specific hydrocarbon groups with the same structure in the branched sections of the hydrocarbon chain.

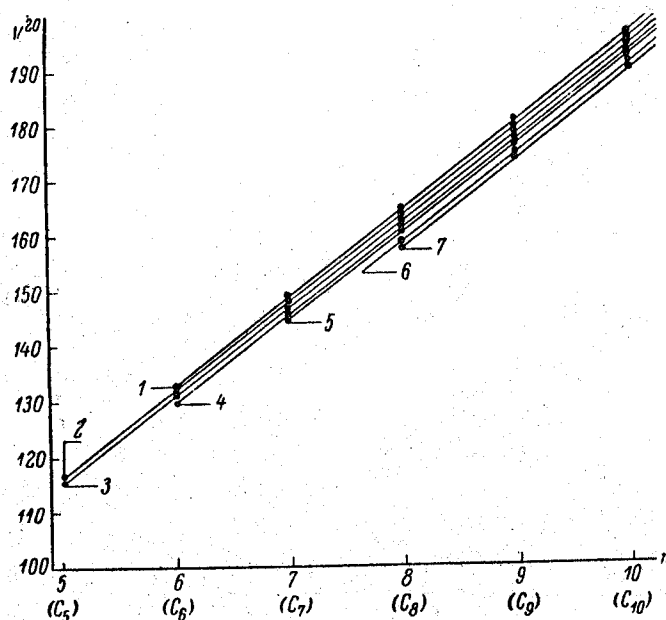


Fig. 1. Molar volumes V^{20} as a function of the number of carbon atoms (n) in alkane molecules of various groups.

1) 2,2-Dimethylalkanes; 2) 2-methylalkanes; 3) n-alkanes;
4) 3-methylalkanes; 5) 3,3-dimethylalkanes; 6) 3,4-dimethylalkanes; 7) 2,3,3-trimethylalkanes.

*For communication I see [3].

Values of Constants $\alpha^{(m)}$ and $\beta^{(m)}$ for Various Physicochemical Properties of Some Homologous Alkane Groups

Alkane group	$V^{(20)}$ ml/mole		$\Delta H_{(el.)}$ (kcal/mole)		L° vap. (kcal/ mole), $t = 130-170^{\circ}$		Log P_{60} (mm of Hg)		$d_4^{(20)}$			t_b		
	α	β	α	β	α	β	α	β	A	B	n_0	t_0	B	n_0
n-Alkanes	34.04	16.108	-10.25	-4.95	1750	857	5.322	-0.428	0.8496	-1.2875	0.7647	782.18	16402	17.98
2-Methylalkanes	37.02	15.838	12.58	4.86	1843	811	5.401	-0.421	0.8526	-1.3795	0.92	822.93	18724	18.55
3-Methylalkanes	33.31	16.069	-11.57	-4.91	2041	784	5.307	-0.412	0.8682	-1.5915	1.8	934.97	25591	23.56
3-Ethylalkanes	29.76	16.270	-9.92	5.06	—	—	5.084	-0.383	—	—	—	2683.02	265104	95.38
2,2-Dimethyl- alkanes	37.40	15.888	16.36	4.68	1516	789	5.452	-0.406	0.8548	-1.4224	0.9172	983.95	28701	24.72
2,3-Dimethyl- alkanes	30.63	16.22	23.05	3.51	1805	791	5.184	-0.389	0.8503	-1.2410	1.0	1246.52	50390	36.56
2,4-Dimethyl- alkanes	31.90	16.38	—	—	—	—	—	—	—	—	—	—	—	—
3,3-Dimethyl- alkanes	32.84	15.98	17.09	4.44	1604	792	5.201	-0.383	—	—	—	1603.43	87344	50.56
3,4-Dimethyl- alkanes	31.41	15.95	—	—	—	—	—	—	—	—	—	—	—	—
2,(n-1)Dimethyl- alkanes	37.00	15.98	13.93	4.91	581	921	5.569	-0.425	—	—	—	818.62	18380	17.90
2,2,(n-1)-Tri- methylalkanes	34.99	15.98	—	—	785	840	6.879	-0.562	—	—	—	—	—	—
2,2,3,3-Tetra- methylalkanes	20.00	16.61	—	—	—	—	—	—	—	—	—	—	—	—

In the present work it is shown that theoretical predictions were actually borne out by experimental data covering various physicochemical properties of paraffin hydrocarbons (alkanes).

According to the theory [3], all the alkanes can be separated into groups on the basis of identical structure in branched fragments of hydrocarbon chains. Examples of such groups are listed in the Table. Then, for each (for example n -th) alkane group some physicochemical dimension P (from among the ones listed above) should be a linear function of the number of carbon atoms (n) in the alkane molecule of that group,

$$P_n^{(m)} = 2P_{12} - 3P_{22} + \Delta^{(m)} + P_{22} \cdot n, \quad (1)$$

with a constant coefficient P_{22} .

Equation (1) can be rewritten in a shorter form,

$$P_n^{(m)} = \alpha^{(m)} + \beta \cdot n, \quad (2)$$

where: $\alpha^{(m)}$ = constant for a given group, β = constant for all the groups. In Figs. 1-4 we have shown to what degree is linear dependence (1), (2) of different physicochemical properties fulfilled in each alkane group. It is evident from these figures that the agreement between theory and experiments is completely satisfactory. The values of group constants $\alpha^{(m)}$ were calculated from experimental data and are listed in the Table; in going from group to group we can see a change not only in $\alpha^{(m)}$ (as theoretically expected) but also an insignificant one in β , although theoretically it should remain constant for all the groups. However, these variations in β are

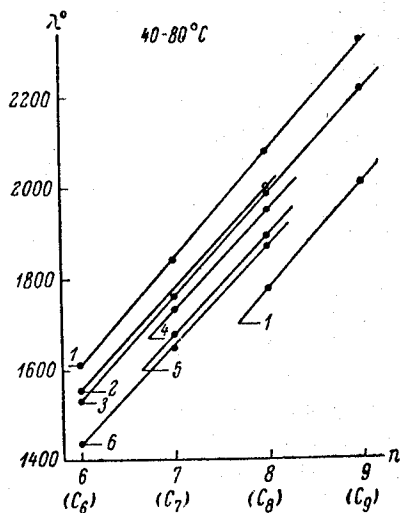


Fig. 2. $\lambda^0 = \frac{L^0}{4.575}$ as a function of the number

of carbon atoms in alkane molecules of various groups.

1) n-Alkanes; 2) 3-methylalkanes; 3) 2-methylalkanes; 4) 2,3-dimethylalkanes; 5) 3-ethylalkanes; 6) 2,2-dimethylalkanes; 7) 2,2(n-1)-trimethylalkanes.

Value of λ^0 are in the interval 40-80°.

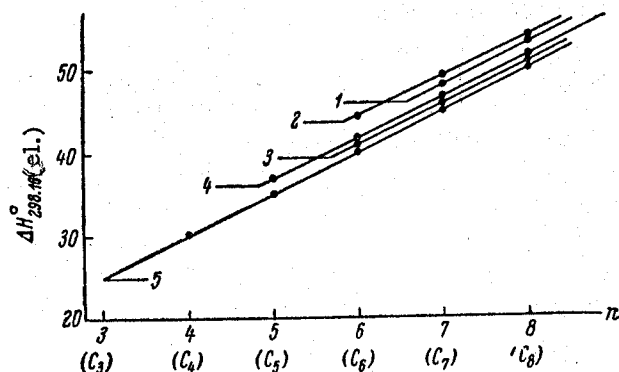


Fig. 3. $\Delta H^0_{(e.l.)}$ gas at $T = 298.16^\circ K$ as a function of the number (n) of carbon atoms in alkane molecules of various groups.

1) 2,(n-1)-Dimethylalkanes; 2) 2,2-dimethylalkanes; 3) 3-methylalkanes; 4) 2-methylalkanes; 5) n-alkanes.

negligible and its value is very close to constant (as the theory would require).

For such factors as density and boiling point of hydrocarbons in each group we derived [3] equations of the type:

$$d_n^{(m)} = \frac{a^{(m)} + b \cdot n}{g^{(m)} + h \cdot n} \quad (3)$$

For calculations it is convenient to change it to this form:

$$d_n^{(m)} = A^{(m)} + \frac{B}{n_0^{(m)} + n}, \quad (4)$$

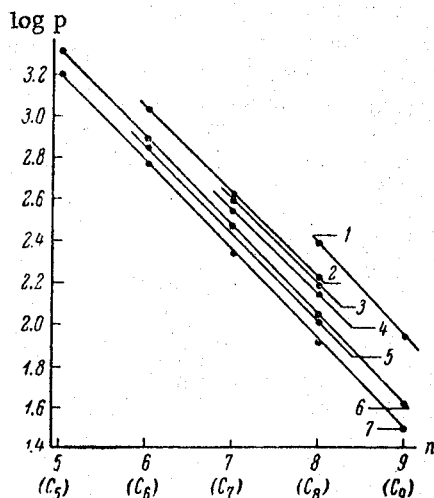


Fig. 4. The logarithm of vapor pressure (at constant temperature 60°) as a function of the number of carbon atoms in alkane molecules of various groups.

- 1) 2,2,(n-1)-Trimethylalkanes; 2) 2,2-dimethylalkanes; 3) 2,(n-1)-dimethylalkanes; 4) 3,3-dimethylalkanes; 5) 3-methylalkanes; 6) 2-methylalkanes; 7) n-alkanes.

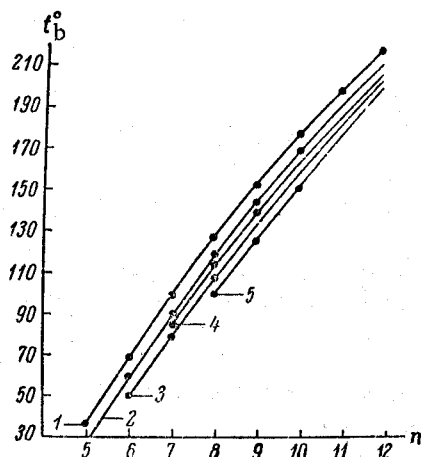


Fig. 6. Boiling point t_b as a function of the number of carbon atoms (n) in alkane molecules of various groups.

- 1) n-Alkanes; 2) 2-methylalkanes; 3) 2,2-dimethylalkanes; 4) 3,3-dimethylalkanes; 5) 2,2,(n-1)-trimethylalkanes.

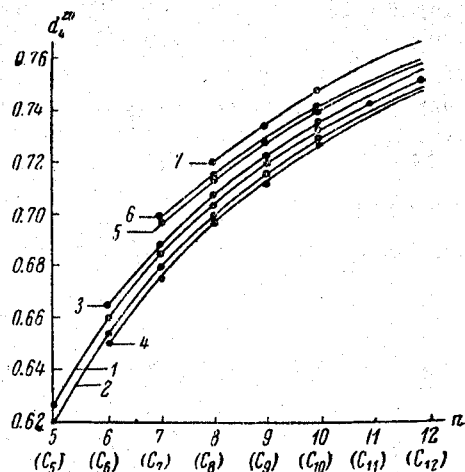


Fig. 5. Density d_4^{20} as a function of the number of carbon atoms in alkane molecules of various groups.

- 1) n-Alkanes; 2) 2-methylalkanes; 3) 3-methylalkanes; 4) 2,2-dimethylalkanes; 5) 2,3-dimethylalkanes; 6) 6-ethylalkanes; 7) 3,4-dimethylalkanes.

where the new constant $A^{(m)}$, B , $n_0^{(m)}$ can easily be expressed through constants $a^{(m)}$, b , $g^{(m)}$, and n . Similarly, for the boiling point of m -th group hydrocarbons the following equation can be derived:

$$t_n^{(m)} = t_0^{(m)} + \frac{B}{n_0^{(m)} + n} \quad (5)$$

Comparisons of experimental data on d_4^{20} and t_b (at 760 mm) (for some alkane groups) with results calculated using Formulas (4) and (5) are shown in Figs. 5 and 6. The constants which enter these equations were calculated from experimental data and are listed in the Table.

It is evident from Fig. 4 that Equations (4) and (5) for d_4^{20} and t_b give a satisfactory description of regularities in each alkane group.

The above described regularities can readily be used to calculate physicochemical properties of as yet unstudied hydrocarbons of a given group, if corresponding experimental data is available for other hydrocarbons of the same group; this undoubtedly is of substantial interest in a number of practical cases. For example, we can use the constants from the Table in Formulas (2), (4) and (5) to calculate physicochemical properties of higher hydrocarbons belonging to groups listed in the same Table.

LITERATURE CITED

- [1] V. M. Tatevskii, Chemical Structure of Hydrocarbons and Regularities in Their Physicochemical Properties, Izd. MGU (1953).*
- [2] V. M. Tatevskii, Proc. Acad. Sci. USSR 109, 131 (1956).**
- [3] V. M. Tatevskii, Proc. Acad. Sci. USSR 113, 836 (1957).**
- [4] Ref. Physicochemical Properties of Hydrocarbons, M.D. Talicheeva ed., Nos. 3, 4, and 5, State Thermotech. Press (1949-1954).*
- [5] F. D. Rossini, Selected Values of Properties of Hydrocarbons, Washington (1953).

Received June 1, 1957

Moscow State University

*In Russian.

**Original Russian pagination. See C. B. Translation.