Appendix

We derive at first equations 4 and 6 for a binary solution.

The frequency of contacts between two groups u and v in a given binary mixture is, according to the model discussed before, equal to

$$Z^{\mathrm{uv}} = 0.5N[n_1{}^2m_1{}^{\mathrm{u}}m_1{}^{\mathrm{v}}s^{\mathrm{u}}s^{\mathrm{v}} + n_1n_2(m_1{}^{\mathrm{u}}m_2{}^{\mathrm{v}} + m_1{}^{\mathrm{v}}m_2{}^{\mathrm{u}})s^{\mathrm{u}}s^{\mathrm{v}} + n_2{}^2m_2{}^{\mathrm{u}}m_2{}^{\mathrm{v}}s^{\mathrm{u}}s^{\mathrm{v}}]$$
$$= 0.5N(n_1m_1{}^{\mathrm{u}} + n_2m_2{}^{\mathrm{u}})(n_1m_1{}^{\mathrm{v}} + n_2m_2{}^{\mathrm{v}})s^{\mathrm{u}}s^{\mathrm{v}} \qquad (11)$$

where N is a proportionality factor. The total frequency of contacts

$$Z = \sum_{\mathrm{uv}} Z^{\mathrm{uv}} = 0.5N[\sum_{\mathrm{u}} s^{\mathrm{u}}(n_1m_1{}^{\mathrm{u}} + n_2m_2{}^{\mathrm{u}})]^2 \qquad (12)$$

is an extensive quantity, *i.e.*, homogeneous of first degree in n_1 and n_2. From the model one concludes that Z is changed by doubling n_1 in the same way as by doubling $m_1{}^{\mathrm{u}}$ or the cross sections of all groups in component 1. Moreover, the frequency of contacts is not changed if one molecule is replaced by another with the same molecular cross section (eq. 3). For these reasons, Z can contain n_1 and n_2 only as the sum of $n_1m_1{}^{\mathrm{u}}s^{\mathrm{u}}$ and $n_2m_2{}^{\mathrm{u}}s^{\mathrm{u}}$. Thus

$$Z = n_1\sum_{\mathrm{u}} m_1{}^{\mathrm{u}}s^{\mathrm{u}} + n_2\sum_{\mathrm{u}} m_2{}^{\mathrm{u}}s^{\mathrm{u}} \qquad (13)$$

except for an irrelevant constant factor, and

$$N = 1/\sum_{\mathrm{v}} s^{\mathrm{v}}(n_1m_1{}^{\mathrm{v}} + n_2m_2{}^{\mathrm{v}}) \qquad (14)$$

The contribution of all uv contacts to the heat content is, according to (11) and (14), if we specialize for one mole of the solution

$$H^{\mathrm{uv}} = 0.5C^{\mathrm{uv}}s^{\mathrm{u}}s^{\mathrm{v}}(x_1m_1{}^{\mathrm{u}} + x_2m_2{}^{\mathrm{u}})(x_1m_1{}^{\mathrm{v}} + x_2m_2{}^{\mathrm{v}})/\sum_{\mathrm{w}} s^{\mathrm{w}}(x_1m_1{}^{\mathrm{w}} + x_2m_2{}^{\mathrm{w}}) \qquad (15)$$

For one mole of the pure component 1 we obtain

$$H_1{}^{\mathrm{uv}} = 0.5C^{\mathrm{uv}}s^{\mathrm{u}}s^{\mathrm{v}}m_1{}^{\mathrm{u}}m_1{}^{\mathrm{v}}/\sum_{\mathrm{w}} s^{\mathrm{w}}m_1{}^{\mathrm{w}} \qquad (16)$$

The corresponding contribution to the relative molal heat content is given by

$$L^{\mathrm{uv}} = H^{\mathrm{uv}} - x_1H_1{}^{\mathrm{uv}} - x_2H_2{}^{\mathrm{uv}} \qquad (17)$$

We abbreviate

$$s_1 = \sum_{\mathrm{w}} s^{\mathrm{w}}m_1{}^{\mathrm{w}};\ s_2 = \sum_{\mathrm{w}} s^{\mathrm{w}}m_2{}^{\mathrm{w}} \qquad (18)$$

From equations 15 to 18 one obtains in lengthy but elementary calculation

$$L^{\mathrm{uv}} = -0.5C^{\mathrm{uv}}s^{\mathrm{u}}s^{\mathrm{v}}(m_1{}^{\mathrm{u}}/s_1 - m_2{}^{\mathrm{u}}/s_2)(m_1{}^{\mathrm{v}}/s_1 - m_2{}^{\mathrm{v}}/s_2)x_1x_2s_1s_2/(x_1s_1 + x_2s_2) \qquad (19)$$

For further simplification we write

$$B^{\mathrm{u}} = s^{\mathrm{u}}(m_1{}^{\mathrm{u}}/s_1 - m_2{}^{\mathrm{u}}/s_2) \qquad (20)$$

and note that according to the definition (20)

$$\sum_{\mathrm{u}} B^{\mathrm{u}} = 0 \qquad (21)$$

We indicate by an accent that the summation over u should not be extended to v = u and conclude from (21) that

$$B^{\mathrm{v}} = -\Sigma' B^{\mathrm{u}} \qquad (22)$$

The partial molal heat content is obtained by summation of (19)

$$L = \sum_{\mathrm{uv}} L^{\mathrm{uv}} = -0.5\sum_{\mathrm{uv}} C^{\mathrm{uv}}B^{\mathrm{u}}B^{\mathrm{v}}x_1x_2s_1s_2/(x_1s_1 + x_2s_2) \qquad (23)$$

The sum can be written as

$$\sum_{\mathrm{uv}} C^{\mathrm{uv}}B^{\mathrm{u}}B^{\mathrm{v}} = 2\sum_{\mathrm{uv}}{}' C^{\mathrm{uv}}B^{\mathrm{u}}B^{\mathrm{v}} + \sum_{\mathrm{u}} C^{\mathrm{uu}}(B^{\mathrm{u}})^2 + \sum_{\mathrm{v}} C^{\mathrm{vv}}(B^{\mathrm{v}})^2 \qquad (24)$$

Introducing (22) into the last two terms by writing

$$(\mathrm{B}^{\mathrm{u}})^2 = -B^{\mathrm{u}}\sum_{\mathrm{v}}{}' B^{\mathrm{v}};\ (B^{\mathrm{v}})^2 = -B^{\mathrm{v}}\sum_{\mathrm{u}}{}' B^{\mathrm{u}} \qquad (25)$$

we obtain

$$\sum_{\mathrm{uv}} C^{\mathrm{uv}}B^{\mathrm{u}}B^{\mathrm{v}} = 2\sum_{\mathrm{uv}}{}'(C^{\mathrm{uv}} - 0.5C^{\mathrm{uu}} - 0.5C^{\mathrm{vv}})B^{\mathrm{u}}B^{\mathrm{v}} \qquad (26)$$

We define the group interaction coefficient by (1) and obtain from (23) and (26) the final result for the molecular interaction coefficient as anticipated in (2) and (4). The accent in the summation symbol in (4) can be omitted in view of (1), but it will be understood that each superscript combination uv is taken only once.

The extension from a binary solution to a multicomponent solution is justified by the fact that the model takes into account only binary contacts so that the heat content can be obtained by simple superposition.

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[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Group Interaction. II. A Test of the Group Model on Binary Solutions of Hydrocarbons

BY M. N. PAPADOPOULOS AND E. L. DERR[1]

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The method of group interaction, which furnishes a model for predicting heats of mixing of non-electrolytes, has been tested on available data of binary solutions of hydrocarbons. It was found that for the cases tested, which comprised dilute binary systems exhibiting wide ranges of deviation from ideality, the model correctly predicts the relative partial molal heat contents of components.

According to the group interaction model presented in the preceding paper,[2] the limiting partial molal heat contents $\bar{L}_1{}^0$ and $\bar{L}_2{}^0$ of the components of a non-associated binary liquid mixture are described by two sets of quantities, namely, a set of *group cross sections* s^{u} and a set of group *interaction coefficients* k^{uv}. The model furnishes the relations

$$\bar{L}_1{}^0 = A_{12}s_1,\ \bar{L}_2{}^0 = A_{12}s_2 \qquad (1)$$

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[1] Paper presented at the Symposium "Recent Advances in the Chemical Thermodynamics of Hydrocarbons and Related Substances," Division of Petroleum Chemistry, American Chemical Society, Chicago, September, 1958.

[2] O. Redlich, E. L. Derr and G. J. Pierotti, THIS JOURNAL, **81**, 2283 (1959).

$$A_{12} = -\sum_{\mathrm{uv}} k^{\mathrm{uv}}(m_1^{\mathrm{u}}/s_1 - m_2^{\mathrm{u}}/s_2)(m_1^{\mathrm{v}}/s_1 - m_2^{\mathrm{v}}/s_2)s^{\mathrm{u}}s^{\mathrm{v}} \quad (2)$$

$$s_1 = \sum_{\mathrm{u}} m_1^{\mathrm{u}}s^{\mathrm{u}},\ s_2 = \sum_{\mathrm{v}} m_2^{\mathrm{v}}s^{\mathrm{v}} \quad (3)$$

where m_1^{u}, m_2^{v} are the numbers of groups u, v in molecules 1, 2 and s_1, s_2 the *molecular cross sections* of molecules 1, 2.

Inspection of relation 1 shows that the cross sections can be examined separately from the interaction coefficients by means of the relation

$$\bar{L}_1^0/\bar{L}_2^0 = s_1/s_2 \quad (4)$$

the ratio of molecular cross sections being directly given by experimental quantities. Thus, a set of group cross sections s^{u} can be tested by means of (4). After the group cross sections s^{u} have been established, the interaction coefficients k^{uv} can be separately examined by means of (2) and (1).

There are not many data available for a systematic check of these relations. As a first step, heat contents for a sufficient set of binary hydrocarbon mixtures have been obtained from the temperature dependence of limiting activity coefficients γ_1^0 and γ_2^0 according to

$$\bar{L}_1^0 = 2.3R\partial(\log \gamma_1^0)/\partial \frac{1}{T}$$

$$\bar{L}_2^0 = 2.3R\partial(\log \gamma_2^0)/\partial \frac{1}{T} \quad (5)$$

Group Volumes.—The cross section of a characteristic group, which is important as a factor in determining the collision frequency of two groups, obviously may be expected to be related to the volume of the group. For this reason, the molal volumes of hydrocarbons were systematically studied and a set of group volumes was established.

TABLE I

GROUP VOLUMES AND CROSS SECTIONS[a]

Type	Group	Group no.	V^{u} (ml.)	s^{u}
Paraffinic	CH_3	3	32.30	1.59
	CH_2	2	16.15	1
	CH	1	0	0
	C	0	−16.15	0
Naphthenic	CH_2	7	18.60	1.10
	CH	6	2.50	0.29
	C	5	−13.65	0
Aromatic	CH	9	14.90	0.95
	C	8	0	0
Polycyclic	CH	9a, b, c	14.90	0.95
	C	8a, b, c	2.50	0.29
Olefinic	$=CH_2$	13	29.80	1.51
	=CH—	12	13.65	0.89
	$=\underset{\mid}{\mathrm{C}}—$	11	0	0
Dienic	=C=	14	11.15	0.79
Acetylenic	≡CH	16	27.30	1.42
	≡C—	15	11.15	0.79

[a] a, b, c are bi-, tri- and tetracyclic types, respectively.

Numerous relations exist for predicting hydrocarbon molecular volumes on the basis of a few empirical parameters pertaining to the carbon number and to the structure and type of a hydrocarbon molecule. Of these, the most successful is due to Kurtz,[3] who has arrived at a relation involving such parameters and an empirical constant. Because of this constant, Kurtz's relation cannot be used to derive group volumes.

TABLE II

MOLAL VOLUMES OF HYDROCARBON LIQUIDS AT 20°

Type	No. of compd. tested	Mol. wt. range	Av. dev., in molal vol., obsd. − calcd., %
Paraffins	506	72–563	1.65
Cyclanes[a]	100	70–589	1.61
Olefins[b]	283	56–559	1.47
Aromatics[c]	190	78–583	1.45
	1079	Grand av.	1.56

[a] 5- and 6-membered rings. [b] Mono-, di-, cycloölefins and acetylenes. [c] Mono-, di- and naphthenoaromatics.

TABLE III

CROSS SECTION RATIO TEST

System	S_1/S_2	V_1/V_2	$\bar{L}_1^0/\bar{L}_2^0$	$(V_1/V_2)^{2/3}$
Benzene$_{(1)}$–heptane$_{(2)}$	0.697	0.606	0.742 ± 0.05	0.718
Benzene$_{(1)}$–cyclohexane$_{(2)}$	.864	.822	.867 ± .01	.877
Toluene$_{(1)}$–heptane$_{(2)}$	.775	.725	.773 ± .01	.807
Toluene$_{(1)}$–cyclohexane$_{(2)}$	.961	.976	1.0 ± .05	.984

TABLE IV

GROUP INTERACTION COEFFICIENTS[a]

Group pair	Designation	k^{uv} (335°K.)
CH_{3p}–CH_a	39	168
CH_{3p}–CH_{2n}	37	34
CH_{2n}–CH_a	79	157

[a] $k_{39} = \frac{1}{2}k_{39a} = \frac{1}{3}k_{39b} = \frac{1}{4}k_{39c}$. $k_{i9} = k_{i8}$, $k_{i2} = k_{i3}$, $k_{i6} = k_{i7}$. Subscripts: p = paraffin, n = naphthene; a = aromatic.

In accord with the group interaction model one would assume that the volume of a molecule is the sum of the volumes of its characteristic groups. Although such an assumption is certainly crude, it has been found that it represents the volumes of over 1000 hydrocarbons as well as Kurtz's and other systems do over a much more limited number of hydrocarbon liquids. A few independent parameters determine the set of group volumes shown in Table I. It can be seen from this table that the group volumes of all types other than paraffinic can be generated from the latter by means of small changes accounting for unsaturation or ring formation.

The types, number and molecular weight range of hydrocarbons whose volumes were used to test the set of group volumes of Table I, together with the average of the absolute values of the deviations for each type, appear in Table II. The experimental molal volumes were taken from the values listed in API Project 44.

Cross Sections.—From dimensional considerations one would expect that the group cross sections are proportional to the $^2/_3$ power of the group

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(3) S. S. Kurtz, "The Chemistry of Petroleum Hydrocarbons," Vol. I, Reinhold Publ. Corp., New York, N. Y., 1954, p. 275.

TABLE V

LIMITING HEAT CONTENTS (L^0) OF HYDROCARBONS–BINARY SOLUTIONS OF HYDROCARBONS

System	s_1	s_2	Temp., °C.	$\log \gamma_1^0$	$\log \gamma_2^0$	$\bar{L}_1^0$, cal. mole^{-1} Obsd. Calorim.	$\bar{L}_1^0$, cal. mole^{-1} Obsd. $d\gamma/dT$	$\bar{L}_1^0$, cal. mole^{-1} Calcd.	$\bar{L}_2^0$, cal. mole^{-1} Obsd. Calorim.	$\bar{L}_2^0$, cal. mole^{-1} Obsd. $d\gamma/dT$	$\bar{L}_2^0$, cal. mole^{-1} Calcd.	Contributions to $\log \gamma_{1,2}^0$ Heat$_{1,2}$	Contributions to $\log \gamma_{1,2}^0$ Entropy$_{1,2}$	FH	Ref.
Benzene(1)–heptane(2)	5.70	8.18	25	0.205	0.310										8, 11, 12, 13, 14
			90	.110	.182										
			57	.158	.246		720^a	630		970^a	900	0.479, 0.645	−0.332, −0.407	−0.047	
Benzene–cyclohexane	5.70	6.60	25	.205	.236										
			80	.140	.161										
			52	.173	.199		570^a	590		660^a	680	0.382, 0.442	−0.209, −0.243	− .008	11, 15, 16, 17
			15–20						800^c		740				9
Naphthalene–heptane	18.18	8.18	60	.487											
			110	.406											
			85	.447			940^b	1250				0.577	−0.139	− .005	8
Anthracene–heptane	10.66	8.18	25	1.097											
			130	0.785											
			77	0.941			1630^b	2000				1.019	− .152	− .002	8
Chrysene–heptane	13.14	8.18	25	1.748											
			130	1.230											
			77	1.489			2710^b	2870				1.692	− .236	− .021	8
Biphenyl–heptane	10.08	8.18	25	0.734											
			130	.343											
			77	.539			2040^b	1560				1.277	− .812	− .001	8
Terphenyl–heptane	14.46	8.18	25	1.415											
			130	0.881											
			77	1.148			2790^b	2740				1.744	− .669	− .043	8
Benzene–biphenyl	5.70	10.08	25	0.053	0.077										
			80	.032	.059										
			52	.043	.068		180^a	0		150^a	0				18, 19, 20, 21
Tetralin–heptane	8.78	8.18	25	.380											
			130	.265											
			77	.323			600^a	510				0.375	− .052	0	8
Benzene–pinene	5.70	8.36	25						900^c		1000				10
p-Xylene–cyclohexane	6.98	6.60	15–20			600^c		350	490^c		330				9
p-Xylene–toluene	6.98	6.34	15–20			10^c		35	10^c		30				9
Cyclohexane–hexane	6.60	7.18	15–20			260^c		280							9
Cyclohexane–heptane	6.60	8.18	25	.053											
			130	.008											
			77	.031			235^a	220				0.147	− .116	−0.014	8, 11, 22
Toluene–heptane	6.34	8.18	25	.155	0.212										
			90	.104	.146										
			57	.130	.179		390^a	380		500^a	490	0.257, 0.332	−0.127, −0.153	−0.02	8, 11, 20, 23, 24

TABLE V (*Continued*)

System	s_1	s_2	Temp., °C.	log γ_1^0	log γ_2^0	L_1^0, cal. mole^{-1}			L_2^0, cal. mole^{-1}			Contributions to log $\gamma^\circ_{1,2}$			
						Obsd.			Obsd.						
						Calorim.	dγ/dT	Calcd.	Calorim.	dγ/dT	Calcd.	Heat$_{1,2}$	Entropy$_{1,2}$	FH	Ref.
Toluene–cyclohexane	6.34	6.60	25	.176	.176										
			80	.124	.124										
			52	.150	.150		455^a	400		455^a	420	0.306, 0.306	−0.156, −0.156	0	8, 11
			15–20			670^c		450	590^c		470				9
Ethylbenzene–heptane	7.34	8.18	25	.212											
			90	.130											
			57	.171		610^b		330				0.413	−0.242	−0.008	8
Benzene–hexane	5.70	7.18	15–20						930^c		890				9
n-Butylbenzene–heptane	9.34	8.18	25	.243											
			90	.143											
			57	.193			750^b	260				0.504	−0.311	0	8
Benzene–toluene	5.70	6.34	15–20			70^c		34	70^c		38				9
n-Butane–*n*-pentane	5.18	6.18	126	.00	0.00										
			203	.00	.00										
			163	.00	.00		0^a	0		0	0	0	0		25
n-Pentane–*n*-heptane	6.18	8.18	126	.00	.00										
			203	.00	.00										
			163	.00	.00		0^a	0		0	0	0	0	0	26
n-Heptane–*n*-hexadecane	8.18	17.18	20			105^d		0	105^d		0				5
			25			95^d		0	95^d		0				5
Isoöctane–*n*-hexadecane	9.18	17.18	25			220^d		0	220^d		0				5
n-Octane–*n*-hexadecane	9.18	17.18	20			75^d		0	75^d		0				5
			30			55^d		0	55^d		0				
			50			30^d		0	30^d		0				
n-Decane–*n*-hexadecane	11.18	17.18	20			45^d		0	45^d		0				5
			30			30^d		0	30^d		0				
			73			15^d		0	15^d		0				
n-Hexane–*n*-hexadecane	7.18	17.18	20			115^d		0	115^d		0				5
n-Hexane–*n*-dodecane	7.18	13.18	20			45^d		0	45^d		0				5
n-Heptane–*n*-dotriacontane	8.18	33.18	73						160^c		0				5

[a] Less than 150 cal. mole^{-1}. [b] Less than 300 cal. mole^{-1}. [c] Less than 50 cal. mole^{-1}. [d] Exp. error estimated to be less than 25 cal. mole^{-1} in $\bar{L}^0$.

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volumes.[4] The group cross sections s^u thus calculated are given in the last column of Table I. The proportionality factor has been chosen so that the cross section of the paraffinic CH_2 group is unity. Zero value, however, has been assigned to the groups with negative values of the group volume V^u, such as C(paraffinic) and C(naphthenic), since the negative values indicate that these groups are deeply embedded and completely shielded by neighbor groups.

Since molecular cross sections are assumed to be the sum of group cross sections (equation 3), their values can be tested experimentally with the aid of equation 4 and known temperature coefficients of the free energy. The results shown in Table III are in agreement with the experimental data within the experimental errors. Even the few available data are sufficient to exclude the assumption of proportionality between volume and cross section (Scatchard–Hildebrand). For the systems under consideration, equation 4 does not differ decisively from Langmuir's assumption that the molecular cross section is proportional to the $^2/_3$ power of the molal volume.

Group Interaction Coefficients.—After the group cross sections were established and tested (Table III), a set of interaction coefficients k^{uv} was obtained from the available data. From the number of groups listed in Table I, it is obvious that the number of interaction coefficients needed is quite large. Certain simplifying assumptions, therefore, must be introduced, and relationships among the various k^{uv}'s sought, so that the number of these empirical constants is reduced. First, it seems reasonable that within groups of the same type, the interactions would be similar in character. For example, the interaction of the paraffinic group CH_3 (group number 3) with a given group u is probably similar to the interaction of the other paraffinic groups with the same group u. Similarly, the interactions of the various aromatic (mono-, di-, tri and tetra-) groups with a given group v would be simply related to each other (see Table IV). Likewise, interaction between paraffinic groups is assumed to be negligible. The model, therefore, does not represent the rather small effects found for paraffin mixtures by van der Waals and Hermans.[5]

Next, since several groups in Table I have been assigned cross sections equal to zero, no interaction coefficients are needed for such groups.

Finally, the equality of the volumes of isomeric paraffins suggests the possibility that isomeric paraffins interact identically with any kind of molecule. Therefore, the rule has been adopted to replace any paraffin or paraffinic branch by its normal isomer.

These simplifications now lead to a comfortably small number of interaction coefficients k^{uv}, which have been derived from a few selected binary mixtures. Their values appear in Table IV. These coefficients were used in calculating the temperature dependence of the limiting activity coefficients γ_0 of all available binary systems by means of equation 2, 3, and 5. The comparison of these data and directly determined heats of mixing with the results based on the cross sections and interaction coefficients of Tables I and IV is shown in Table V. Crude estimates of the experimental uncertainties are given in the footnotes to Table V. It can be seen that the group interaction model predicts satisfactorily the heats of mixing for all of these solutions, several of which exhibit extreme deviations from ideality. The average deviation in $\bar{L}^\circ$ of 120 cal. is well within the experimental errors involved; for example, a deviation of 200 cal. in the heat is equivalent to a deviation of only 2% in each of two terminal γ°'s measured over a temperature range of 50°.

On the basis of the limited range of data in Table V, it has been tentatively concluded that the interaction coefficients k^{uv} are proportional to $1/T$.

Entropy of Mixing.—The entropy contributions to the observed values of the logarithm of the limiting activity coefficients are shown in the next to the last column of Table V. For comparison, the entropy contributions calculated by means of the relation of Flory and Huggins for chain molecules

$$(\log \gamma^0)_{FH} = \log (V_1/V_2) - (1 - V_1/V_2)/2.303 \quad (6)$$

are shown in the last column. The discrepancies are large, and the entropy terms themselves make substantial contributions to the total free energy. At present there is no satisfactory way of systematically predicting these entropy effects. Satisfactory results obviously cannot be obtained with cell models that do not take into account structural details or distinguish between molecular volume and available free volume in the liquid state. Following Hildebrand,[6] we are studying the relation of these entropy effects with both the molecular (van der Waals) volume and the free volume[7] in the standard state, in the hope that the latter would be a controlling factor of the rotational restriction of hydrocarbon molecules in the liquid state, and, hence, a principal effect contributing to the excess entropy of solution.

Part of the evidence presented in this paper has been drawn from a critical review by Dr. C. Black and Mrs. E. King, to whom the authors wish to express their sincerest thanks.

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(4) This is reasonable for non-polar groups, which interact over a very short range (van der Waals force). It cannot, however, be expected to be true of polar groups (non-hydrocarbon). This subject is treated in a following paper dealing with the application of the group method to polar systems.

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