EMPIRICAL CALCULATIONS ON INTERACTION ENERGIES OF CLUSTERS OF MOLECULES: THE CORRELATION WITH HEATS OF VAPOURIZATION*

P.Hobza[a], R.Stružinský[b], N.Duc Thang[c] and R.Zahradník[c]

[a] *Institute of Hygiene and Epidemiology,*
Center of Industrial Hygiene and Occupational Diseases, 100 42 Prague 10
[b] *Institute of Microbiology, Czechoslovak Academy of Sciences,*
Laboratory for Cell Membrane Transport, 142 20 Prague 4 and
[c] *J. Heyrovský Institute of Physical Chemistry and Electrochemistry,*
Czechoslovak Academy of Sciences, 121 38 Prague 2

Optimal geometries of 26 types of model clusters were determined by means of the Buckingham potential with the Eliel's parameter set. 28 types of molecules were treated. Pair, total and partial interaction energies were estimated. The latter are given by the sum of pair energies for the interactions between the central molecule and the surrounding molecules. The partial interaction energies were found to be linearly correlated with the heats of sublimation and heats of vapourization.

The calculations of the interaction energy in clusters of molecules are topical for several reasons, one of them being that the clusters studied in this paper may be taken as models of molecular crystals. This makes it possible to compare the calculated interaction energies with the heats of sublimation. Some information can also be obtained, though on a very simple level, about the structure of the nearest surrounding of a particular molecule in liquids. It is to be noted, however, that such an approach disregards the motion of molecules in liquids, though the statistical averaging can be performed *a posteriori*. Its another shortcoming is due to the neglect of vacancies. Nevertheless some properties of liquids should be, in a rough approximation, accounted for by this model.

Since our major goal in the future is the calculation of partition coefficients and energies of solvation, we prefer the discontinuous model of the liquid to the continuous one.

The heats of vapourization were calculated by means of both the discontinuous[1] and continuous[2-4] models, by making use of the Kitaygorodsky's potential in all cases. With polar molecules, the Coulomb and induction terms were involved, too. Good agreement between predicted and experimental heats of vapourization was found for both polar and nonpolar molecules.

The subject of this paper is the calculation of interaction energies in clusters of molecules. In contrast to ref.[1], the emphasis is laid on the determination of stabilities of various geometry arrangements of clusters for a series of molecules of dif-

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fering structures. The prime aim is the comparison of the calculated interaction energies with the observable counterparts — with the heats of vapourization and heats of sublimation. The paper is also oriented to the solvation phenomena, in particular to the problem of the search for the procedures suitable for the description of the solvation processes, where it is necessary to know at least the structure of the first solvation shell.

CALCULATION

Computation of interaction energies. Once the structure of a cluster of molecules has been suggested and a suitable computational method has been selected, the calculation of the interaction energy is straightforward.

The empirical potential has been used throughout. Its use was dictated by the set of systems treated which comprises clusters containing as much as 15 molecules which in turn may be composed of as much as 18 atoms. We are aware that the empirical potential is not well-suited for the determination of the geometry of clusters[5] because it assigns to clusters geometries that are sometimes different from those predicted by more sophisticated methods.

It is known that the parameter set of Kitaygorodsky[6] gives rather good estimates of the interaction energy for systems composed from C and H atoms, *i.e.* from atoms for which the parametrization was made. The interaction energies of hydrocarbons should therefore be well accounted for by this parameter set. Since the molecules studied contained also other than C and H atoms (*e.g.* S, Cl, O, F), we made use in all calculations of the Eliel's parametrization[7] of the Buckingham potential (Eq. (*1*))

$$F(r) = b \cdot \exp(-ar) - cr^{-6}, \tag{1}$$

where $F(r)$ is the potential, r is the intersystem distance, and a, b, c are constants.

The empirical potential is formed only by two terms. The first term stands for the repulsion energy, the second one for the dispersion energy. For this reason we selected such systems for which the other energy terms in the perturbation expansion (Coulomb, induction, and charge-transfer terms) are negligible. Generally, this applies to uncharged, nonpolar or weakly polar systems.

The interaction energy for two molecules A and B can be expressed as a sum o interactions over all atoms in molecules A and B:

$$E_{AB} = \sum_i^{n_A} \sum_j^{n_B} b_{ij} \cdot \exp(-a/D_{ij}) - \sum_i^{n_A} \sum_j^{n_B} c_{ij}(D_{ij})^{-6}, \tag{2}$$

where $a = 13 \cdot 587$, $b_{ij} = 828\,000 \cdot e_{ij}$, $c_{ij} = -2 \cdot 25 \cdot e_{ij}$,
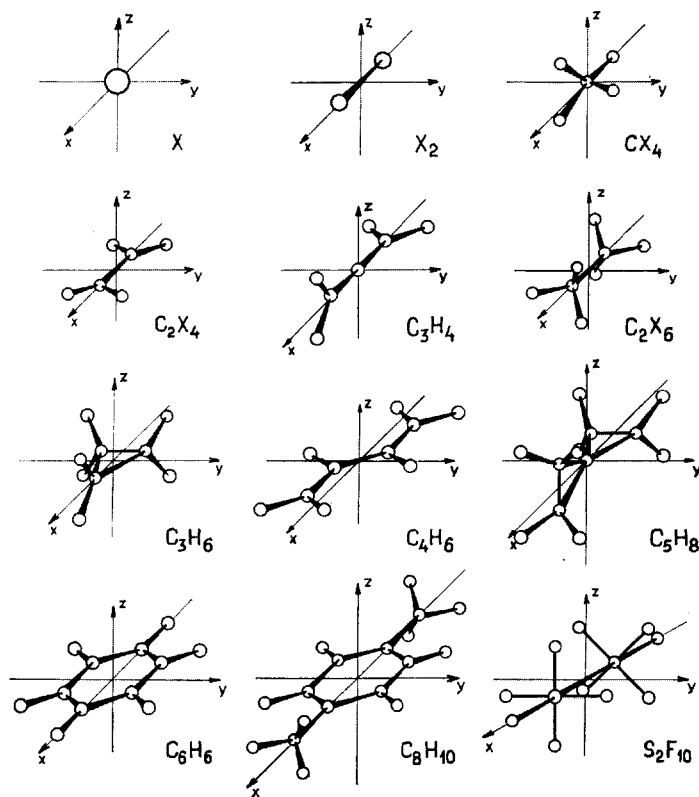
$$D_{ij} = r_{ij}/(R_i + R_j),$$

FIG. 1

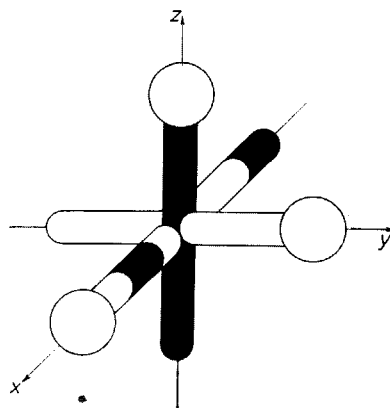Fundamental Orientation of Molecules or Types of Molecules in the Cartesian Coordinate System

FIG. 2

Fundamental Orientation of the Symbol Replacing a Molecule in the Cartesian Coordinate System

where r_{ij} is the distance between the i-th atom of the molecule A and the j-th atom of the molecule B; R_i and R_j are the van der Waals radii for the atoms i and j, n_A and n_B are the numbers of atoms in the molecules A and B. The numerical values of the e_{ij} and R_i parameters for the H, C, N, O, F, S, Cl, Br, and I atoms were taken from ref.[7]. For the noble gases, the e_{jj} constants were obtained by the following formula

$$e_{jj} = e_{ii} R_j/R_i, \tag{3}$$

where e_{ii} means the parameter for the foregoing element in the respective row of the periodical system. The van der Waals radii for the noble gases were taken from ref.[8].

Summation over pair interaction energies (2) gives the total interaction energy, E^T, for the system of N molecules

$$E^T = \sum_{K=1}^{N} \sum_{L=K+1}^{N} E_{KL}. \tag{4}$$

The partial interaction energies, E^P, are given by the summation over the pair interaction energies between the central molecule $(K = 1$ in Eq. $(4))$ and the other surrounding molecules.

$$E^P = \sum_{L=2}^{N} E_{1L}. \tag{5}$$
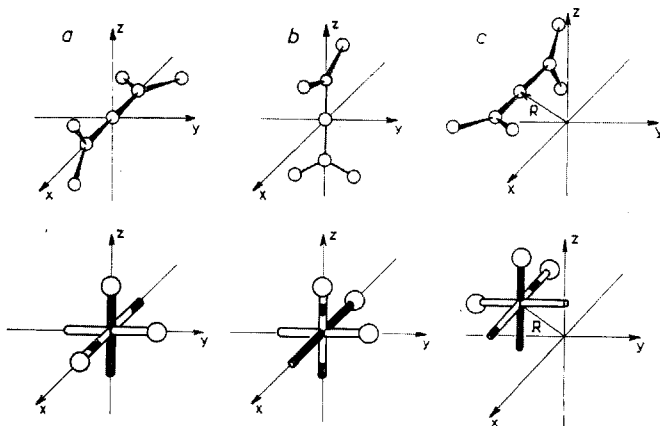

FIG. 3

Operation with a Molecule and Its Assigned Symbol

a) The fundamental orientation, b) 90° clockwise rotation round the y axis, c) 180° clockwise rotation round the z axis and a subsequent displacement of the centre by a distance R.

Molecules studied and their geometries. The set of molecules studied comprises monoatomic molecules (He, Ne, Ar, Kr, Xe), biatomic molecules (H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2), methane and its halogene derivatives (CF_4, CCl_4, CBr_4), ethylene (C_2H_4), tetrafluoroethylene (C_2F_4), tetrachloroethylene (C_2Cl_4), allene (C_3H_4), ethane (C_2H_6), hexafluoroethane (C_2F_6), cyclopropane (C_3H_6), 1,3-butadiene (C_4H_6), spiropentane (C_5H_8), benzene (C_6H_6), 4-xylene (C_8H_{10}), and decafluoro disulfide (S_2F_{10}).

The cartesian coordinates of these molecules were calculated from the reported experimental bond lengths and angles[9]. The molecules studied are outlined in Cartesian coordinate system in Fig. 1.

Geometries of model clusters. Since it would be difficult to express graphically the structural features of a particular molecule in the cluster, each molecule is substituted by a symbol. The fundamental orientation of the symbol (Fig. 2) corresponds to the fundamental orientation of any other molecule in Fig. 1. Rotation and displacement of a molecule is expressed by an analogous rotation and displacement of the assigned symbol (Figs 3a, 3b, 3c). This must be kept in mind for a correct understanding of Fig. 4 which presents the structures of clusters.

Altogether we considered 26 model clusters; 23 of them are presented in Fig. 4. To each model a label is assigned which represents the cluster in Tables. The clusters of radial structures 19−21 formed by 10, 11, and 12 molecules are omitted in Fig. 4 because they were constructed in a completely analogous way as the clusters of the same type (15−18) having 6−9 molecules: the molecules lie in the centre and in the apices of the respective regular polygon in the YZ plane.

Symbols R_i ($i = 1, 2, ...$) stand for the nonequivalent distances between the midpoint of the central molecule and the midpoints of the surrounding molecules. The same symbols enter also the Tables with the computed interaction energies.

RESULTS AND DISCUSSION

The optimal surroundings for the systems studied are given in Table I. By the optimal surroundings, we imply such a structure for which the partial interaction energy is maximal. The partial interaction energy for each cluster was estimated in the minimum of the total interaction energy. We performed two types of calculations: either all R_i ($i = 1, 2, 3, 4$) were fixed at the same value, or (in most cases) nonequivalent R_i were subjected to optimization. As example of the optimization treatment we present in Table II the results for benzene for all considered structures*. The entries of Table III are the pair interaction energies for the optimal geometries of pairs of molecules from the studied set.

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* Similar data for the other molecules studied are available from the authors on request.
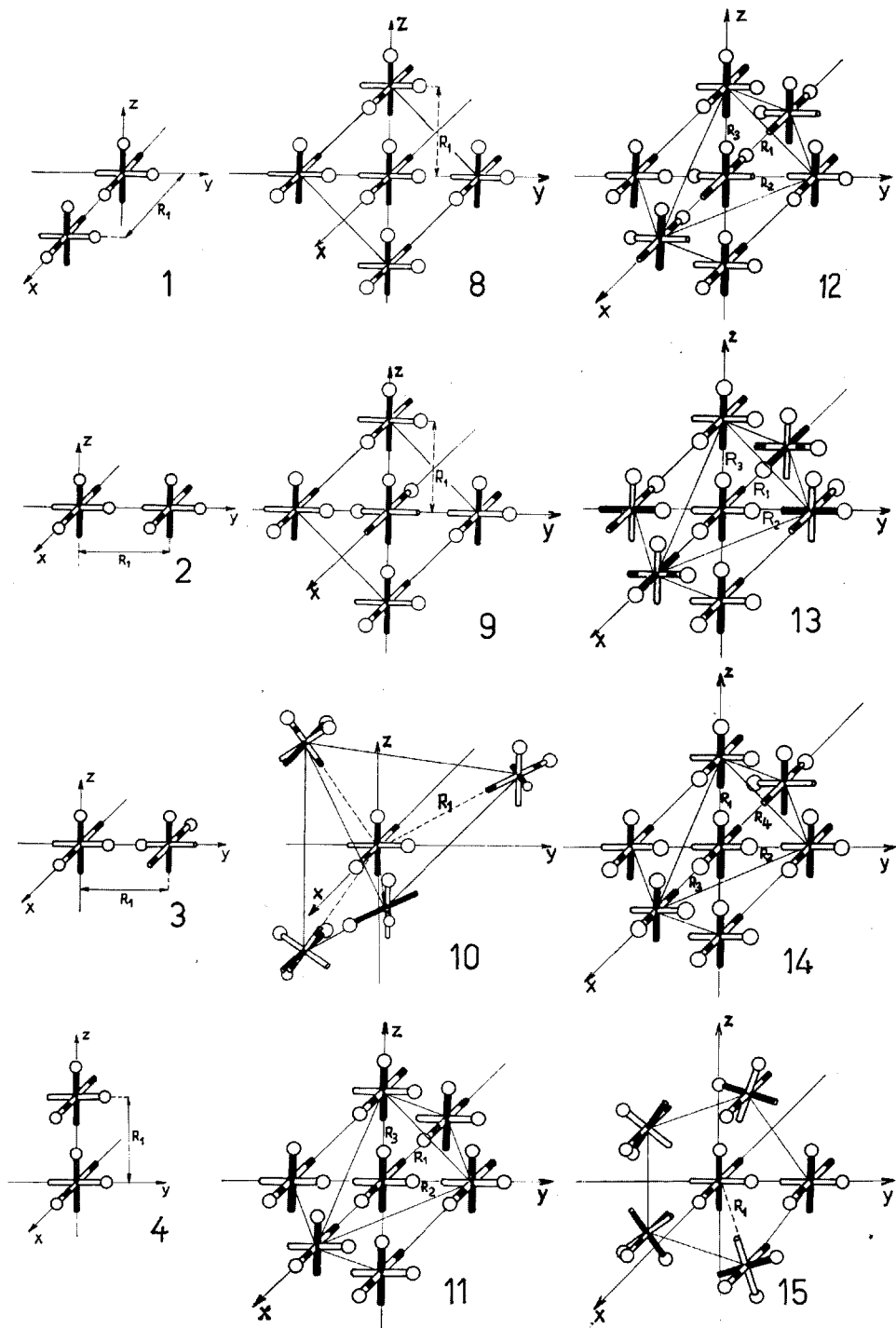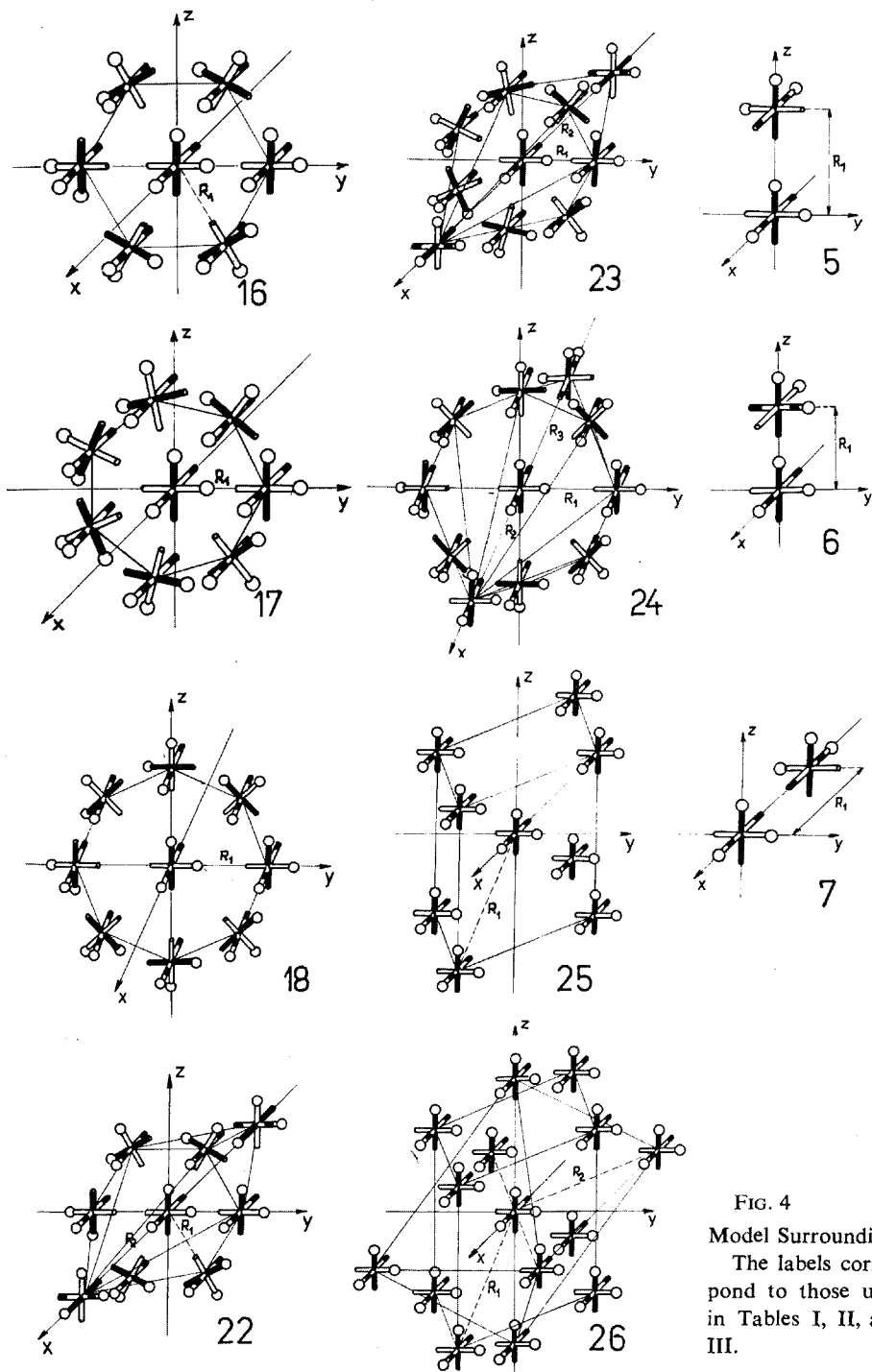
FIG. 4

Model Surroundings
The labels correspond to those used in Tables I, II, and III.

The comparison of heats of sublimation and heats of vapourization (Tables IV and V) shows that these quantities are related by a close linear dependence. This finding is useful for the purposes of comparisons of experimental and calculated data — the less abundant heats of sublimation may be substituted by the heats of vapourization.

TABLE I

Total Interaction Energies (E^T) and Partial Interaction Energies (E^P) for the Optimal Model Surrounding of the Central Molecule

System	Structure[a]	Mode of calculation[b]	$10^{10} R_i$ (m)[a]	E^T, kJ/mol	E^P, kJ/mol
He	26	0	1·9, 2·5	— 4·778	— 1·287
Ne	26	0	2·2, 3·0	— 14·012	— 3·678
Ar	26	0	3·1, 4·1	— 40·321	— 10·941
Kr	26	0	3·4, 4·5	— 60·592	— 16·431
Xe	26	0	3·8, 5·1	— 90·676	— 24·246
H_2	22	0	2·4, 2·6	— 13·594	— 6·100
N_2	22	0	2·9, 3·3	— 30·372	— 13·083
O_2	22	0	2·7, 3·2	— 36·062	— 15·690
F_2	22	0	2·6, 3·2	— 32·238	— 13·963
Cl_2	22	0	3·5, 4·2	— 91·512	— 38·434
Br_2	22	0	3·8, 4·6	—123·842	— 51·781
I_2	22	0	4·2, 5·2	—174·205	— 74·274
CH_4	25	N[c]	3·8	— 35·104	— 15·958
CF_4	14	0	4·6, 4·3, 4·2, 3·2	— 29·388	— 21·112
CCl_4	24	0	6·7, 5·4, 4·2	—120·072	— 48·133
CBr_4	14	0	6·8, 6·3, 5·9, 4·6	— 71·734	— 55·923
C_2H_4	24	0	4·0, 4·1, 4·1	— 90·998	— 34·606
C_2F_4	13	0	3·0, 3·7, 4·0	— 72·496	— 44·041
C_2Cl_4	13	0	3·4, 4·5, 4·7	—178·799	—104·261
C_3H_4	22	0	3·6, 4·5	— 93·902	— 39·421
C_2H_6	22	0	4·1, 4·0	— 63·973	— 32·539
C_2F_6	11	0	4·9, 4·6	— 57·354	— 44·539
C_3H_6	12	0	4·3, 4·4, 3·6	— 62·337	— 45·380
C_4H_6	13	0	4·7, 4·0, 3·0	— 89·471	— 53·626
C_6H_6	13	0	4·6, 4·6, 3·1	—134·277	— 81·650
S_2F_{10}	25	N[c]	5·6	—161·084	— 67·079
C_5H_8	12	0	5·5, 4·3, 4·3	— 89·207	— 65·622
C_8H_{10}	13	0	6·0, 4·5, 3·4	—175·527	—119·148

[a] cf. Fig. 4. [b] 0 all R_i were subjected to optimization; N all R_i were fixed at the same value. [c] With the structure 25 the geometry optimization of the cluster deteriorated the cubic structure.

TABLE II

Total (E^T) and Partial (E^P) Interaction Energies for Various Clusters of Benzene

Structure[a]	Mode of calculation[b]	$10^{10} R_i$ (m)[a]	E^T, kJ/mol	E^P, kJ/mol
1	0	7·1	— 2·243	— 2·243
2	0	6·4	— 4·510	— 4·510
4	0	3·1	— 21·786	—21·786
6	0	3·1	— 21·916	—21·916
8	N	6·4	— 11·606	—10·824
10	N	4·7	— 45·317	—41·999
11	N	6·9	— 12·330	—10·640
11	0	7·0, 6·4, 3·1	— 67·986	—56·911
13[c]	0	4·6, 4·6, 3·1	—134·277	—81·651
25	N	6·3	— 52·982	—14·397
15	0	6·2	— 20·389	—16·790
16	0	6·3	— 27·874	—18·539
17	0	6·1	— 51·769	—23·937
18	0	6·1	— 80·211	—21·476
19	0	6·0	—137·143	—26·844
20	0	6·1	—179·816	—31·091
21	0	6·4	—206·154	—30·648

[a] cf. Fig. 4. [b] 0 all R_i were subjected to optimization; N all R_i were fixed at the same value. [c] Optimal configuration.

TABLE III

Optimal Pair Interaction Energies

System	Structure[a]	$10^{10} R$, m[a]	E, kJ/mol
He	1	1·9	— 0·130
Ne	1	2·2	— 0·381
Ar	1	3·1	— 1·100
Kr	1	3·4	— 1·683
Xe	1	3·8	— 2·464
H_2	6	2·4	— 0·950
N_2	6	2·9	— 2·029
O_2	6	2·7	— 2·456
F_2	6	2·5	— 2·310
Cl_2	6	3·3	— 6·443
Br_2	6	3·6	— 8·899
I_2	6	3·9	—12·736
CH_4	7	3·1	— 3·946

TABLE III (*continued*)

System	Structure[a]	$10^{10} R$, m[a]	E, kJ/mol
CF_4	7	3·3	− 8·314
CCl_4	7	4·3	−16·472
CBr_4	7	4·7	−20·786
C_2H_4	4	3·1	− 5·171
C_2F_4	6	3·0	−10·000
C_2Cl_4	6	3·4	−24·631
C_3H_4	6	3·1	− 8·314
C_2H_6	6	3·3	− 8·033
C_2F_6	6	3·7	−12·493
C_3H_6	5	3·6	−10·903
C_4H_6	6	3·0	−13·489
C_6H_6	6	3·1	−21·916
S_2F_{10}	3	4·9	−13·221
C_5H_8	3	4·3	−11·590
C_8H_{10}	6	3·0	−34·041

[a] *cf.* Fig. 4.

TABLE IV

Heats of Vapourization at the Boiling Point, Heats of Sublimation at 0 K and Normal Boiling Points

System	H_{1-g} kJ/mol	$H_{0,s-g}$ kJ/mol	T, K
He^c	0·10	0·059	4·2
Ne^b	1·76	1·920	27·1
Ar^a	6·53	7·812	87·3
Kr^c	9·04	11·192	120·0
Xe^c	12·64	15·857	165·1
$H_2{}^b$	0·92	0·796	20·4
$N_2{}^c$	5·56	6·935	77·3
$O_2{}^c$	6·82	8·817	90·2
$F_2{}^a$	6·53	8·353	85·1
$Cl_2{}^c$	20·42	30·166	239·1
$Br_2{}^a$	31·05	46·50	331·4
$I_2{}^a$	43·47	74·08	456·0
$CH_4{}^a$	8·24	9·186	111·5
$CF_4{}^a$	13·05	17·38	145·2
$CCl_4{}^b$	30·00	41·97	349·8
$CBr_4{}^b$	43·51	—	460·2

TABLE IV (continued)

System	H_{1-g} kJ/mol	$H_{0,s-g}$ kJ/mol	T, K
$C_2H_4{}^a$	13·56	18·985	169·5
$C_2F_4{}^b$	16·82	—	197·6
$C_2Cl_4{}^b$	34·69	—	394·2
$C_3H_4{}^c$	20·92	—	239·6
$C_2H_6{}^a$	14·69	20·12	184·1
$C_2F_6{}^b$	16·15	—	194·4
$C_3H_6{}^b$	20·04	29·59	240·3
$C_4H_6{}^b$	22·59	—	268·8
$S_2F_{10}{}^b$	29·29	—	302·2
$C_6H_6{}^b$	30·75	49·74	353·3
$C_5H_8{}^b$	33·39	—	312·2
$C_8H_{10}{}^a$	36·40	—	411·5

[a] Taken from ref.[10]. [b] Taken from ref.[11]. [c] Taken from ref.[12].

TABLE V

Statistical Characteristics of the Dependences of the Optimal Pair Interaction Energies (I), Partial Interaction Energies of the Optimal Surroundings (II) and Experimental Heats of Sublimation (III) on Experimental Heats of Vapourization[a]: $y = Ax + B$

Correlation[b]	N^c	A	B	$S^{a,d}$	$S_A{}^d$	$S_B{}^{a,d}$	r^e
I. B	5	−0·183	0·045	0·112	0·011	0·083	0·995
I. C	7	−0·275	0·642	0·220	0·006	0·125	0·999
I. D	16	−0·621	−0·951	4·964	0·126	3·271	0·796
I. A	28	−0·533	−0·600	4·780	0·072	1·626	0·825
II. B	5	−1·810	0·440	1·037	0·100	0·761	0·995
II. C	7	−1·590	4·404	1·261	0·032	0·714	0·999
II. D	16	−2·066	4·598	17·638	0·448	11·621	0·777
II. A	28	−2·012	2·598	13·947	0·209	4·745	0·884
III. B	5	1·263	−0·219	0·178	0·017	0·131	1·000
III. C	7	1·692	−2·644	2·371	0·061	1·343	0·997
III. D	7^f	1·700	−4·591	2·856	0·139	2·77	0·984
III. A	19^f	1·658	−2·855	2·412	0·048	0·885	0·993

[a] All energy data in kJ/mol. [b] Meaning of letters: B monoatomic molecules, C biatomic molecules, D polyatomic molecules, A the whole set. [c] Number of members. [d] Standard error [e] Correlation coefficient. [f] Data only for CH_4, CF_4, CCl_4, C_2H_4, C_2H_6, C_3H_6, C_6H_6.
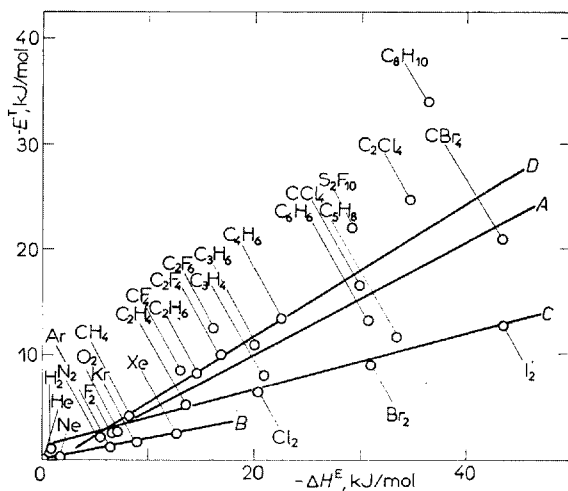
FIG. 5

Optimal Pair Interaction Energies Plotted against Experimental Heats of Vapourization. For Statistical Characteristics See Table V

A correlation line for the whole set of molecules, B, C, D correlation lines for mono, di, and polyatomic molecules.
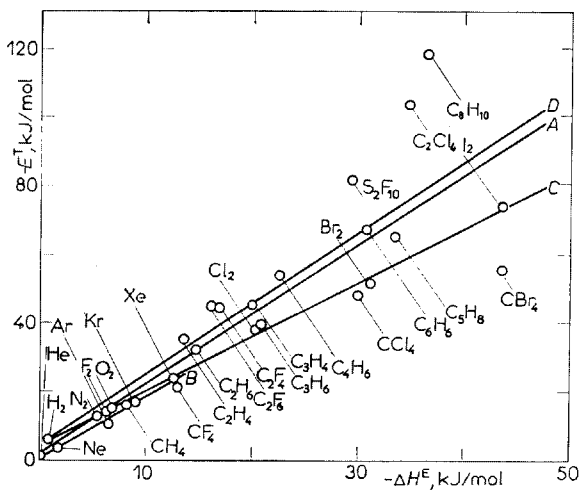

FIG. 6

Optimal Partial Interaction Energies Plotted against the Experimental Heats of Vapourization. For Statistical Characteristics See Table V

A correlation line for the whole set of molecules, B, C, D correlation lines for mono, di, and polyatomic molecules.

The plot of the pair interaction energies against the heats of vapourization (Fig. 5) shows a split into three partial dependences; the first for monoatomic molecules, the second for biatomic molecules and the third for polyatomic molecules. The slopes range from 0·18 to 0·62. They differ the more from unity the higher is the number of the molecules in the nearest surrounding of the central molecule. Differing slopes suggest that the situation can hardly be improved by adopting a single model for the nearest surrounding of the treated molecule. The calculations performed for the structure 11 provided the support for this assumption: a similar split into partial dependences is observed as in the case where only pair interactions were considered. Hence it was inevitable to find the optimal surrounding for each molecule under study. The interaction energies obtained in this way are plotted in Fig. 6 against the heats of vapourization. Compared to Fig. 5, the plot is now more compact, though a split into three partial dependences is still notable. The range of slopes is smaller $(1·59 - 2·06)$. The circumstance that the slopes are higher than unity is probably due to the neglect of vacancies of the liquid in the theoretical approach. Actually, this is also found in the correlation of the heats of sublimation with the heats of vapourization (Table V). If the slopes of these dependences are used as correction factors for accounting for vacances, the slopes of correlations lie in the range of $0·94 - 1·43$, rather close to the unit slope.

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Translated by P. Čársky.