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Abstract

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On the Interaction of Valence-Unbound Carbon and Hydrogen Atoms

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§ 1. **Introduction.** For many problems of physical chemistry, the most expedient approach to a molecule is as a system of interacting atoms. For numerous applications of such a theory to various questions of reactivity, kinetics, adsorption, thermochemistry, etc., it is necessary to have information on the energy curves of interaction of valence-unbound atoms. In what follows we assume that there is no difference between the interaction curves of valence-unbound "neutral" atoms belonging to the same or to different molecules.

§ 2. **Universal interaction curve of C and H atoms.** The best-known experimental parameters of interaction curves are the intermolecular distances in a crystal. These distances are undoubtedly universal ([1]) (at least to an accuracy of about 5%) for all hydrocarbons, and indeed for all organic substances in general, regardless of their chemical nature. Taking into account that, upon entry into a crystal, a slight "compression" of the molecules occurs, we shall take as the equilibrium distances of "isolated" atoms: C···C 3.8 Å; C···H 3.15 Å and H···H 2.6 Å. These values lead us to equilibrium intermolecular distances in the condensed phase of C···C 3.6 Å and H···H 2.35 Å, i.e., to the average experimental values.

Let us denote by $z = r/r_0$ the ratio of the distance between atoms to their equilibrium distance and transform the expression of the 6-exp potential $A/r^6 + B\exp\{-r/\rho\}$ to the form

$$U = U_{2/3}\left[\frac{1}{z^6} - \frac{6}{\alpha}e^{\alpha}e^{-\alpha z}\right] \Big/ \left[11.4 - \frac{6}{\alpha}e^{\frac{1}{3}\alpha}\right],$$

where $U_{2/3}$ is the value of the energy at $r = \frac{2}{3}r_0$ ($\frac{2}{3}r_0$ is a typical shortening encountered in organic molecules. For example, in aliphatic chains the carbon atoms attached to one and the same atom are at distances of about $\frac{2}{3}r_0$). The parameter $\alpha = r_0/\rho$, the parameter

$$U_{2/3} = \frac{A}{r_0^6}\frac{11.4 - 6e^{\alpha/3}/\alpha}{1 - 6/\alpha},$$

and the parameter B has been eliminated, as usual, by the equilibrium condition

Fig. 1

Figure 1: Fig. 1

$$B = \frac{6A}{\alpha r_0^6} e^{\alpha}.$$

The transformation we have carried out substantially facilitates the search for unknown parameters and gives the problem much greater clarity.

We see that $U/U_{2/3}$ is a function of only one parameter α. The second parameter is readily chosen as a scale quantity. Without detailed analysis it is obvious that $U_{2/3}$ is a quantity of the order of units of kilocalories per mole. It is very important that a reasonable interval of values of α is also evident. Indeed, calculating $U/U_{2/3}$ for $z = 1$, we immediately see that the values of the interaction energy at equilibrium (which chiefly determine the heats of sublimation) will be reasonable only for α lying within the limits 11-18. Thus, the advantages of the new notation for the 6-exp potential lie in the small scatter of possible values of the two parameters (the third parameter r_0 has already been introduced into the formula).

The curve $U/U_{2/3}$, as is evident from Fig. 1, for any α is fixed at the point $z = 2/3$ and has a fixed abscissa of the minimum (at $z = 1$). Since the value of $U/U_{2/3}$ at the minimum is small, the curve is in essence fixed at two points. As a result, variation of α does not play a special role; the curve is only slightly sensitive to the parameter α, as is quite clearly seen from the figure.

The parameters α and $U_{2/3}$ for hydrocarbons were chosen by us so as to satisfy the known experimental data in the best possible way.

It is interesting that the values of α and $U_{2/3}$ for all three interactions are apparently very close to one another. At this initial stage of the investigation we consider it possible to use the universal expression (in the coordinates given)

$$U = 3.5\left(-0.04/z^6 + 8.6 \cdot 10^3 \cdot e^{-13z}\right). \tag{1}$$

The choice $\alpha = 13$ determines the value of the other two coefficients standing in the parentheses. The value $U_{2/3} = 3.5$ kcal/mole is chosen independently.

Thus, in relation to our previous work ([2]), the following step forward has been made. In the previous work the expression $U'(\Delta r/r)$ was assumed to be universal. The present investigation indicates the possibility of using a universal curve not only for the derivative of the energy, but also for the energy itself. The expression U'/C, used earlier, agrees well with the corresponding expression used in this work.

Fig. 1

Fig. 2

Figure 2: Fig. 2

Fig. 2

§ 3. **Intermolecular interactions.** Figure 2 shows the curve, calculated by us with the aid of formula (1), of the lattice energy of crystalline methane. The curve leads to values, coinciding with experiment, of the lattice constant (5.8 Å) and of the lattice energy (the experimental value, calculated from the heat of sublimation, is 2.6 kcal/mole). The asymmetry of the curve also leads to a reasonable course of the lattice parameter with changing temperature.

The energy of methane in the gas-crystalline state (so we call the state of a substance in which the centers of the molecules form a regular lattice, while the azimuths of the molecules with respect to the crystallographic axes are disordered) turns out, to an accuracy of 0.2 kcal/mole, to be the very same. The calculated energy of a quasicrystalline assembly of molecules, as well as of molecules arranged in short-range order, does not differ in any substantial way from the energy of the crystal. This is already clear from the fact that the energy changes little with variation of the lattice parameter from 0° K to the melting temperature.

It must be thought that the last result is of a very general character: the potential energy of interaction of molecules for an organic substance-

properties at absolute zero only slightly lower than the potential energy of interaction of molecules at the evaporation temperature of the liquid. In other words, the heat supplied to the substance goes mainly into changing the energy of motion of the molecules.

The equilibrium values of the lattice energies were also calculated for other substances [3]. Thus, for the gas-crystalline state of cyclopentane the calculation gave 7 kcal/mol instead of the value 8 kcal/mol obtained from the experimental value of the heat of sublimation. It is interesting that for gas-crystalline cyclohexane the calculated and experimental values differ substantially (respectively 3 and 9.6 kcal/mol). This discrepancy is interpreted as follows. The calculation was made under the assumption of complete disorder in the azimuths of the molecules. However, cyclohexane molecules differ substantially in their shape from a sphere. The presence of short-range order excludes such an arrangement of neighbors in which the largest diameters of the molecules lie on one line. The overestimation of "close" situations in the calculation naturally leads to an increase in repulsion and, consequently, to an increase in the energy (a decrease in absolute value).

The calculation of the lattice energy of benzene is very cumbersome. We calculated the contribution to the energy from the interaction of a molecule with the 12 nearest neighbors forming the first coordination sphere. This gives 6.5

kcal/mol. On the basis of less cumbersome calculations, carried out for gas-crystalline substances, it is known to us that the contribution to the energy of the first coordination sphere amounts to 80-85%. Since the experimental value of the lattice energy of benzene is 9-10 kcal/mol, the agreement between calculation and experiment is excellent here as well.

Our curve for the energy of interaction of atoms practically coincides with the curve of interaction of carbon atoms found by Crowell [4] in analyzing the properties of graphite. It also follows from our curve that the observed decrease in distances in the crystal between aromatic molecules with an increase in their sizes should occur.

In addition to estimating the energy and the equilibrium distance, the interaction curves can be used to obtain compressibility values. The calculation of the compressibility for methane led to the value 0.31 kcal/mol $\cdot$ Å^3, as against the experimental value 0.26.

§ 4. **Intramolecular interactions.** In order to estimate the strain energy of a molecule

$$W_{\text{str}} = \frac{1}{2}\sum C\alpha_i^2 + \sum U_{ik},$$

it is necessary to find the force constant of the ideal angle C (see (2)). The value of C for a carbon atom can be selected using data on the optical force constant γ. By definition, $\gamma = [\partial^2 W/\partial\alpha^2]_{\alpha=\alpha_0}$, where α_0 is the equilibrium value, and W is the elastic energy of the ideal angle plus the interaction energy of valence-unbonded atoms. To convert values of C into values of γ, one must know the form of the interaction curve, since

$$\gamma = \partial^2 W/\partial\alpha^2 = C + U'(r)\,\partial^2 r/\partial\alpha^2 + U''(r)\,(\partial r/\partial\alpha)^2.$$

The value $C = 35$ kcal/mol, in combination with the expression for our potential, leads to the values $\gamma_{\text{CCC}} = 95$ kcal/mol, $\gamma_{\text{HCH}} = 79$ kcal/mol, in complete agreement with the optical data. Using this value of C, we calculated the values of the strain energies, as well as the optimal conformations of a number of hydrocarbon molecules. The experimental and calculated data are summarized in Table 1.

The data on conformations are close to the results of our previous work. The new approach made it possible also to calculate the magnitudes of the strain energy. As can be seen from the table, the main contribution to the strain energy is made by the repulsion of valence-unbonded atoms, and not by the deviation of the angle from the tetrahedral value. Thus, even in cyclobutane $\frac{1}{2}C\alpha^2 = 2$ kcal/mol, whereas the strain energy per CH_2 group is 21 kcal/mol. Reason-

Table 1

Molecule	Angles	Angle magnitudes, deg.: theory, present work	Angle magnitudes, deg.: theory, ([2])	Angle magnitudes, deg.: experiment	Strain energy per CH_2 group, kcal/mol	Excess strain energy, compared with alkanes: theory	Excess strain energy, compared with alkanes: experiment
Ethane	HCH	109.4	–	109.3	–	–	–
Alkanes	CCC	112	111.5	112	18	–	–
Alkanes	HCH	110	108	–			
Cyclopropane	HCH	116.5	118	118.2	23	5	10
Cyclobutane	HCH	113	112	114	21	3	7
Cyclopentane	HCH	110.5	109	–	18.5	0.5	1
Cyclohexane	CCC	112.5	112				
Cyclohexane	HCH	110	108	–	18	0	0
Nortricyclene	θ	98.5	96	96.5	–	–	
Nortricyclene	β_1	112	121	–			
Nortricyclene	β_2	113	112	–			
Norcamphane	α_1	114	109.5	–	–	–	
Norcamphane	α_2	103	103*				
Norcamphane	α_3	91	92				
Norcamphane	β_1	106	108.5				
Norcamphane	β_2	112	107.5*				
Norcamphane	β_3	114	113*				

* The values of the angles α_2, β_2, β_3 in ([2]) were erroneous.

there is a similar situation; it is a consequence of another, as it seems to us, more correct definition of strain energy. In the classical literature, strain energy is understood as the excess strain energy compared with alkanes. This excess strain energy amounts to $^2/_3$ of the energy associated with violation of the tetrahedral character of the valencies.

Attention is drawn to the fact that the calculated values of the excess strain energies are substantially smaller than the experimental (calorimetric) values. It follows from this that one half of the strain is due to a change in the magnitude of the energy of interaction of valence-bonded atoms (bond strain).

The examples given show that the proposed universal potential gives reasonable results when applied to the calculation of many properties of a substance. Further investigations will show the possibility of refining the interaction curves. It seems to us, however, that even such a method of calculation deserves attention, since it makes it possible to predict properties with an accuracy much better than one order of magnitude.

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CITED LITERATURE

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Note: Figure translations are in progress. See original paper for figures.