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Calculations of the Thermodynamic Properties of Polymers

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The methods for the calculation of the thermodynamic parameters of various classes of polymers are examined. Together with a description of the classical phenomenological approaches, much attention has been devoted to the description of computational methods involving the modelling of the properties of polymers on the basis of the corresponding parameters of their low-molecular-weight analogues.
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I. INTRODUCTION

The greatest amount of experimental thermodynamic data which have now accumulated in the chemistry of macromolecular compounds refer to a narrow range of linear vinyl polymers and a very small amount is concerned with polymers of other classes. At the same time a significant proportion of these data require a critical assessment and revision. This applies to a large extent to polymers with a complex structure of the repeating units (carbo-, and hetero-chain polyconjugated systems, cyclochain polymers, systems with a benzenoid structure of their macromolecules, etc.), for which it is frequently very difficult and sometimes impossible to estimate experimentally and accurately the contributions to the properties by various phase states of the chains and to take into account the presence of chemical defects and branches in the macromolecules as well as the influence of all possible impurities associated with the use of catalysts, initiators, etc. in the polymerisation process.

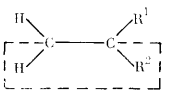
This is why modern theoretical methods for the calculation of thermodynamic properties have come to play an extremely important role in the determination of new thermodynamic characteristics of polymers and in the revision of values already available. The attempts at the employment for the solution of this problem of rigorous quantum-chemical methods, which are based on fundamental physical concepts, have encountered mathematical difficulties which cannot be overcome. This factor led to the creation of phenomenological methods, which in many instances make it possible to carry out the required calculations successfully and comparatively simply.

II. PHENOMENOLOGICAL METHODS

A large number of simple and complex phenomenological computational schemes have now been developed on the basis of many years of systematic studies of the thermodynamic properties of various groups of low-molecular-weight compounds.[1-16] Many of these schemes are used successfully in calculations of the thermodynamic parameters of saturated hydrocarbons, olefins, and the simplest organoelemental compounds. The parameters calculated are the heats of combustion and formation, heats of evaporation and fusion, heat capacities, entropies, etc. However, in relation to polymeric substances, the computational methods for the determination of the above characteristics have not yet been adequately developed. The virtual impossibility of the exact determination of the energies of non-valence and resonance interactions between the atoms in macromolecules and also of taking into account different phase states of the polymers may be indicated as the main cause holding back the application of modern computational schemes in such cases. Several more or less successful attempts at the extension to polymers of certain schemes which had been used earlier to calculate the properties of low-molecular-weight compounds are described below.

On the basis of the assumptions made in the calculation of the properties of polymers, the phenomenological methods can be divided by convention into two main groups. In schemes of the first group,[1-6] it is assumed that each given bond in any molecule or macromolecule has a constant characteristic energy. The overall energy of the molecule is found by the summation of the characteristic bond energies, applying corrections to the sum of the energies for the steric effects corresponding to the interaction of atoms not linked by valence bonds.

Calculations by means of these schemes of properties such as the enthalpies of atomisation and formation, which make it possible to obtain fairly accurate results (±0.1–0.2 kcal) for paraffinic and olefinic hydrocarbons, can be applied in principle to a polymer having the corresponding structure. The carefully developed Allen–Skinner scheme[2-4] has been used[11,16] for this purpose; this represents the structure of the polymer of the ethylene type $-CH_2-C(R^1R^2)-$ by a two-membered unstrained ring



in which the "characteristic" energies of the C–H and C–C bonds (including one C–C bond represented by a dashed line) were adopted in accordance with the data for methane and ethane taking into account corrections for the steric interaction of atoms not linked by valence forces. For example, the enthalpy of atomisation ΔH_a^0 (298) of a hydrocarbon polymer is given by the following expression in terms of this scheme:

$$\Delta H_a^\circ(298) = N_{CC}E_{CC} + N_{CH}E_{CH} + x\alpha_{CCC} - t\beta_{CCC} - s.1, \qquad (1)$$

where N_{CH} and N_{CC} are the numbers of C–H and C–C bonds in the elementary unit of the polymer, E_{CH} and E_{CC} are the C–H and C–C bond energies, α_{CCC} is the interaction energy for a pair of neighbouring atoms linked by valence bonds with the given carbon atom, x the number of such pairs, βCCC the trigonal energy of the interaction between three carbon atoms each of which is the nearest neighbour of the

other two, t the number of trigonal interactions, A the energy of the *gauche*-butane interaction, and s the number of such interactions.

Table 1 presents the results of the calculations in accordance with this scheme of the enthalpies of formation of a group of vinyl polymers and several new carbochain polymers corresponding to the hypothetical gaseous state of the polymer unit. In order to be able to compare the calculated ΔH^0_{form}(298, gas) and experimental heats of formation of the polymers in the condensed phase [ΔH^0_{form}(298, solid)] and also the calculated and experimental heats of polymerisation of the monomers corresponding to these quantities, the authors[11,16] made the not wholly correct assumption that the heat of evaporation (sublimation) of the elementary polymer units is equal to the heat of evaporation of the monomer. By the condensed state, the authors[11,16] understood any state of the solid polymer, ranging from wholly amorphous to partly crystalline.

On comparing the enthalpies of formation of polymers calculated in accordance with this scheme with the experimental quantities, the following conclusions may be drawn.

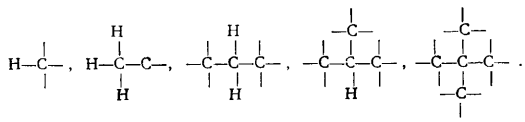
(a) For polyethylene and polymers which are monosubstituted derivatives of polyethylene, the agreement between the calculated enthalpies of formation of the polymers and the quantities found experimentally is entirely satisfactory.

(b) The scheme is altogether inapplicable to the calculation of the enthalpies of formation of 1,1-disubstituted derivatives of polyethylene [polyisobutylene, poly(vinylidene fluoride), poly-α-methylstyrene] and also for polymers characterised by considerable non-valence or resonance interactions (polymers with polar and bulky substituents, polymers with heteroatoms in the main chain, and polymers with conjugated bonds). The schemes of Tatevskii,[10] Laidler,[7] Cox,[8] and Benson[9] can be assigned to the second group of phenomenological schemes, which can be used in the calculation of the thermodynamic properties of polymers. A thermodynamic property ϕ is represented in these schemes by a linear function of the numbers of structural elements or bonds n_i in the repeating units of the polymer:

$$\varphi = \sum_i n_i f_i \ , \qquad (2)$$

where f_i is a characteristic constant referred to the structural element of the polymer unit or to a bond of type i.

These methods do not employ corrections taking into account the non-valence and resonance interactions of the atoms and are therefore simpler and more convenient than the methods in the first group, although they are less accurate. The number of characteristic parameters of the structural elements or bonds in these schemes is much larger, which permits calculations of properties taking into account the first-order sphere around the atoms in the structural element (Tatevskii's scheme[10]) or taking into account the hybrid state of the bonds between the carbon atoms (Laidler's and Cox's schemes[7,8]). For example, on the basis of the classification of the first method (Tatevskii's scheme), it is possible to obtain five types of structural elements and five types of coordination of the atoms (one for H atoms and four for C atoms) for alkanes taking into account the first sphere:



Both schemes indicated can be applied in principle to both carbochain polymers and polymers of other classes. The characteristic parameters of the bonds or groups of bonds are set up on the basis of a statistical treatment of a set of experimental data for different compounds in accordance with Eqn.(2).

Table 1 presents the results of calculations by Cox's method of the enthalpies of formation of a group of heterochain polymers and the corresponding enthalpies of polymerisation. In those cases where experimental data are available for the polymers considered, their comparison with the calculated values reveals considerable discrepancies (polyoxyethylene, polyformaldehyde, polytetrahydrofuran) probably as a consequence of the neglect in the calculations of the contribution of the non-valence interactions of the atoms.

Table 1. Comparison of the thermochemical characteristics of polymers calculated in accordance with the Allen–Skinner and Cox Schemes by Somayajla et al.[11] with the experimental values.

Polymer	$-\Delta H^0_{form}$(298), kJ unit^{-1}			$-\Delta H^0_{pol}$(298), kJ unit^{-1}		Refs.
	calc.		expt.	calc.	expt.	
	(gas)	(cond.)	(cond.)	(gas, gas)	(liq., cond.)	
Polyethylene	41.0	54.4	56.1	93.3	95.0	[53—55]
Polypropylene	67.8	86.2	83.7	88.3	85.8	[55, 56]
Polybut-1-ene	88.3	109.2	—	88.3	—	[45, 57]
Polyisobutene	102.5	123.0	88.7	85.8	51.5	[55]
Polybutadiene	—33.9	—13.0	—16.3	76.1	72.8	[58]
Polysioprene	3.3	28.9	25.1	78.2	74.5	[59]
Polystyrene	—67.4	—22.6	—34.3	85.8	69.9	[60]
Poly-α-methylstyrene	—33.1	14.6	—35.1	84.9	35.1	[61]
Poly(vinyl chloride)	71.5	92.0	94.6	93.3	95.8	[61]
Poly(vinylidene chloride)	109.2	136.4	100.4	111.3	75.3	[61]
Poly(vinylidene fluoride)	415.5	432.6	474.0	84.9	125.5	[61]
Polytetrafluoro-ethylene	789.9	807.9	809.6	154.0	155.6	[4, 11, 63]
Polynitroethylene	37.2	74.9	83.6	82.0	90.8	[64]
Poly(acrylic acid)	396.6	442.7	—	63.2	77.4	[16, 72]
Polyacroleine	148.5	179.1	—	74.1	79.9	[16, 73]
Polyacrylonitrile	—90.0	—57.3	—	94.1	77.0	[16, 74]
Poly(ethyl vinylether)	225.5	—	—	85.4	—	[65]
Poly(vinyl acetate)	405.8	438.5	—	79.5	87.9	[16, 74]
Poly(methyl acrylate)	395.0	428.0	—	72.4	78.7	[66, 75]
Poly(methyl methacrylate)	428.9	464.8	433.5	87.9	56.5	[67, 76]
Poly(maleic anhydride)	508.8	552.7	—	96.2	58.6	[68, 77]
Polyformaldehyde	165.3*	190.0*	171.1	49.4	30.5	[55, 57]
Polyacetaldehyde	200.8*	227.6	—	44.4	—	[69]
Polyoxyethylene	167.4*	193.3*	—	114.6	94.6	[6, 69]
Polyoxystyrene	47.3*	101.7*	—	91.2	—	[66]
Polytetrahydrofuran	208.4*	240.6*	—	24.3	22.2	[69, 78]
Polycyclopropene	106.3	87.4	—	172.4	—	[70]
Polycyclopropane	65.7	86.6	84.1	118.4	115.9**	[71]
Polycyclohexane	131.4	164.4	168.2	8.4	—2.9**	[71]
Polycyclo-octane	164.0	208.8	224.3	39.7	34.7**	[71]
Polyacetylene	—58.6	—41.0	—	—	—	[57]
Polyacetonitrile	—68.6	—33.5	—	—	—	[57]
Polyacetone	244.8	276.6	—	—	—	[69]

*Calculation in accordance with Cox's scheme.
**Estimated theoretically.[16]

The best results were achieved in the calculation of the enthalpies and entropies of polymerisation of monomers with bonds of the type >C=C< and >C=C–C=C<.[12] Depending on the availability of initial experimental data, calculations have been carried out using Eqns.(3) or (4):

$$\left.\begin{aligned} \Delta H^0_{pol}\ (298) = \Delta H^0_c\ (298, \text{M}) - \Delta H^0_c\ (298, \text{P}) = \sum_i n_i^{\text{M}} f_{H,i}^{\text{M}} - \sum_i n_i^{\text{P}} f_{H,i}^{\text{P}}; \\ \Delta S^0_{pol}\ (298) = S^0(298, \text{P}) - S^0(298, \text{M}) = \sum_i n_i^{\text{P}} f_{S,i}^{\text{P}} - \sum_i n_i^{\text{M}} f_{S,i}^{\text{M}}\ ; \end{aligned}\right\} \qquad (3)$$

$$\Delta H^0_{pol}\ (298) = \sum n_{(i\to j)} f_{H(i\to j)},\quad \Delta S^0_{pol}\,(298) = \sum n_{(i\to j)} f_{S(i\to j)} \qquad (4)$$

In Eqn.(3) the quantities $\Delta H_c^0(298, M)$, $S^0(298, M)$, $\Delta H_c^0(298, P)$, and $S^0(298, P)$ are the enthalpies of combustion and the entropies of the monomer and the polymer unit respectively, $f_{H,i}^M$, $f_{S,i}^M$, $f_{H,i}^P$, and $f_{S,i}^P$ are constants for a structural element of type i in the monomer and polymer, and finally n_i^M and n_i^P are the numbers of structural elements of type i in the monomer and polymer. In Eqns.(4) the summation is carried out only over the corresponding pairs of interconvertible structural elements of type i in the monomer and of type j in the polymer and not over all types of structural elements, $f_{(i \to j)}$ being the corresponding constants.

The constants in Eqns.(3) and (4) were calculated from the experimental data for the following physical states (298.16 K, 101.325 kPa): for the gaseous (G) and liquid (L) states in the case of the enthalpy of combustion and only for the gaseous state in the case of the entropy.

Table 2 shows that comparison with the literature data of the enthalpies and entropies of polymerisation, calculated by Eqns.(3) and (4), of compounds such as alkenes, halogeno- and phenyl-alkenes, and styrene, acrylic acid, and methacrylic acid derivatives demonstrates an entirely satisfactory agreement between calculation and experiment. The discrepancies between the calculated and literature data are on average 6.3 kJ mol^{-1} for the enthalpies and 12.5 J mol^{-1} K^{-1} for the entropies.

The above comparison showed that the given scheme can be used to calculate the enthalpies and entropies of polymerisation via the $>C=C<$ and $>C=\overset{|}{C}-\overset{|}{C}=C<$ bonds in the corresponding monomers, for which the change in phase state during the reaction is of three types: monomer (G) → polymer (G), monomer (G) → polymer (S†), and monomer (L) → polymer (S). On the basis of Hess's law, the enthalpies and entropies of polymerisation of the monomers found can be easily converted into the enthalpies of formation and the entropies of the corresponding polymers (subject to the condition that the enthalpies of formation and entropies of the corresponding monomers are known). Unfortunately the method considered does not allow the determination of the given property of the polymer in the crystalline and amorphous-crystalline phases. At the same time the calculations of the thermochemical characteristics of the polymer in the condensed (amorphous) state and in the hypothetical gas phase calculated in this way can hardly ensure a reliable determination of a parameter as important as the energy of cohesion, because the constants employed in the calculation are averaged with respect to different classes of organic compounds and inaccurately reflect the energetic characteristics of specific types of compounds. Furthermore, the classification of different structural elements in the molecules on which the method is based makes it possible to take into account the interaction of atoms only in the immediate environment while long range interactions between atoms, due to the large dimensions of the macromolecules (the molecular weight factor), are completely disregarded.

Together with the difficulties enumerated above, one should also note that the given scheme in the version proposed by Grikina et al.[12] is subject to certain limitations. For example, it cannot be used to calculate the properties of heterochain, cyclochain, and heterocyclic polymers. Naturally, it is necessary to realise clearly that none of the available energy schemes is as yet able to predict correctly and take into account the individual characteristics of separate bonds in the macromolecule for many polymeric systems characterised by structural features such as the steric strain in the chain and bond conjugation.

Thus analysis of many empirical schemes for the calculation of thermodynamic properties of polymers employed nowadays shows in general that their scope is limited. When the structure of the elementary polymer units becomes more complex (for example, when cyclic, heterocyclic, and benzenoid structural elements appear in the polymer chain) the practical application of all the schemes considered becomes more difficult. At the same time, in connection with the vigorous progress in the theoretical and practical branches of polymer chemistry, the need to obtain new thermodynamic data and to test the values already available has arisen in the first place precisely for these complex polymer systems.

Table 2. Comparison with experimental data[16] of the enthalpies and entropies of the polymerisation of monomers via the $>C=C<$ and $>C=\overset{|}{C}-\overset{|}{C}=C<$ bonds calculated[12] by Tatevskii's method.

Monomer	Phase transition	$-\Delta H_{pol}^0(298)$, kJ mol^{-1}		$-\Delta S_{pol}^0(298)$, J mol^{-1}K^{-1}	
		calc.	Ref.16	calc.	Ref.16
$H_2C=C(CH_3)H$	G, G	85.8—87.4	88.3	159.4	166.9
»	G, S	101.3	104.2	—	—
»	L, S	83.3	85.8	113.8	116.3
$H_2C=C(C_2H_5)H$	G, G	87.1 : 84.5	88.3	156.5	166.5
»	G, S	103.3	—	—	—
»	L, S	84.1	83.7**	—	—
$H_2C=C(CH_3)_2$	G, G	78.2÷79.1	85.8	174.0	171.5
»	G, S	72.8	72.0	—	—
»	L, S	55.2	51.5	—	—
H_2C CH—CH CH_2*	G, G	71.5 (*cis*); 75.7 (*trans*)	76.1	133.9 (*cis*); 139.3 (*trans*)	—
»	L, S	65.3 (*cis*); 91.6 (*trans*)	72.8	—	85.8
$H_2C=CH—C(CH_3)$ CH_2*	G, G	71.5	78.2	133.9	—
»	L, S	67.8	74.5	—	101.3
H_2C $CHCl$	L, S	103.3	95.8	—	—
H_2C CCl_2	L, S	73.2	75.3	—	—
$H_2C=C(C_6H_5)H$	L, S	69.0	69.9	106.7	104.6
$H_2C=C(CH_3)COOCH_3$	L, S	56.5	56.5	118.4	117.2
H_2CHC CHC_6H_5	L, S	36.8	35.1***	—	—
$H_2C=CHCOOH$	L, S	77.8	77.4	—	—
$H_2C=CHCOOCH_3$	L, S	77.8	78.7	—	—
$H_2C=C(OCOCH_3)H$	L, S	86.6	87.9	—	—
$H_2C=C(CH_3)COOC_6H_{11}$	L, S	56.5	51.0	—	—
$H_2C=C(CH_3)COOC_6H_5$	L, S	56.5	51.5	—	—

*A double bond in the centre of the monomer unit is formed in the polymer.

**Data of Furukawa and Reilly.[50]

***Data of Dainton and Ivin.[6]

Note. G = gas, L = liquid, S = solid (Ed.of Transaltion).

In order to overcome the difficulties indicated, attempts have been made in the last decade to develop procedures for calculations on the thermodynamics of polymers based on the principle of similarity.[15,18,19] According to this principle, the study of the properties of complex polymers is replaced by the study of the properties of a series of model compounds which reproduce the structure of integral repeating polymer units. Here there is no need to employ a large number of increments other than those necessary to take into account the influence of the two end groups of the model compound on the properties of the repeating units. The practical application of this modelling principle

† S = solid (Ed.of Translation).

provides for the employment of experimental data characterising the given low-molecular-weight model or system of models. On the other hand, the experimental procedures for the determination of thermodynamic data for model substances (combustion, calorimetry, reaction calorimetry, measurements of heat capacity, etc.) are themselves usually less laborious and at the same time more accurate than in the direct investigation of the properties of the polymers themselves.

Different versions of the above modelling method, including the mathematical form of modelling,[40] in which the properties of complex polymers are obtained from those of less complex polymers (the interpolation method) are examined below.

III. MODELLING METHODS

1. The Method of Linear Correlations of the Parameters of Model–Polymer Systems

The methods of similarity theory,[13,14] widely and successfully employed in the chemistry of individual low-molecular-weight compounds, have not as yet been developed adequately in polymer chemistry. A study in which the applicability of the rules of similarity theory to polymers has been demonstrated can be regarded as one of the first steps in this direction.[15]

A modelling method, the essential feature of which consisted in the selection and investigation of the thermodynamic parameters of individual compounds modelling the structure of sections of the macromolecular chains whose length was not less than that of the single repeating elementary unit, has been employed in the determination of the thermodynamic parameters of polymers.[15] Thermodynamic data corresponding to specific sequences of models and polymers investigated previously served as the basis for the calculation of the uninvestigated analogous properties of other polymers. This type of calculation can be performed using a statistical approach[15] in which the correlation coefficient r is used to investigate the interrelation of the properties indicated.

On the basis of general mathematical considerations,[14,20] there should be a linear relation between two functions $f(x, y_1, z_1, \ldots)$ and $f(x, y_0, z_0, \ldots)$, where $y_1, z_1, \ldots$ and $y_0, z_0, \ldots$ are any two sets of fixed values of the arguments y and z, while x is a variable. Here $f(x, y_1, z_1, \ldots)$ cannot be linear with respect to the argument x itself.

The application of this approach to the thermodynamic parameters of any one polymer [$\Delta H_c^0(298)$, $\Delta H_{form}^0(298)$, $S^0(298)$, $\Delta G_{form}^0(298)$, etc.] leads to the expression

$$\varphi_P(x_1, x_2, x_3, \ldots, x_i, \ldots) = \varphi_P^0(x_1^0, x_2^0, x_3^0, \ldots, x_i^0, \ldots) + \sum_i x_i' + \alpha \sum_i \sum_j x_1' x_j' + \alpha^2 \sum_i \sum_j \sum_k x_i' x_j' x_k' + \cdots \quad (5)$$

where x_i', x_j', ... are structural parameters which depend respectively on the arguments x_i, x_j, ...; x_1^0 and x_2^0 are any standard values of the arguments, α is a constant, and $i \neq j \neq k$.

If all the quantities of type x_i' are constant except for x_j', which we shall assume arbitrarily to depend on the nature of the substituent or a group of substituents in the repeating polymer unit, then we obtain the expression

$$\varphi_{P,j} = \varphi_{P,0} + b_P x_j' \quad (6)$$

where $\phi_{P,j}$ and b_P are constants related to parameters of type x_i' corresponding to structural elements whose effect on $\phi_{P,j}$ in a similar series of polymers remains unchanged. The subscript "P" denotes the first combination of constant factors corresponding to the polymer.

On passing to model compounds, it is possible to consider the change in the same quantity x_j' for certain fixed values of the remaining quantities x_i':

$$\varphi_{M,j} = \varphi_{M,0} + b_M x_j' . \quad (7)$$

The subscript "M" denotes the second combination of constant factors corresponding to the model.

From Eqns.(6) and (7), we obtain the expression

$$\varphi_{P,j} = \Delta\varphi_0 + \beta\varphi_{M,j} \quad (8)$$

where $\Delta\phi_0 = \phi_{P,0} - \phi_{M,0}(b_P/b_M)$ and $\beta = b_P/b_M$; it follows from Eqn.(8) that the quantities $\phi_{P,j}$ and $\phi_{M,j}$ depend linearly on one anther, i.e. there is a correlation between them.

It is noteworthy that this conclusion applies to homogeneous interactions in which the chain in the structure of the substituents in the polymer and in the model leads to an additive change in the properties of the system.

Table 3. Parameters of the linear correlation (8) in the studies of Korshak and co-workers[15] and Marchenko[18] describing the relation between the thermodynamic properties of a series of polymers and model compounds.

Characteristic	Phase	N	$\Delta\varphi$	β	r	α, %
Correlation pairs of type (I)						
$\Delta H_{form}^0(298)$, kJ mol^{-1}	(G)-(G)	12	51.664	1.0434	0.9989	0.1
	(L)-(L)	10	48.723	1.0120	0.9997	0.1
	(Cr)-(Cr)	5	55.011	1.0510	0.9947	0.1
	(Φ_j)-(Φ_j)	20	48.149	1.0050	0.9980	0.1
$S^0(298)$, J mol^{-1}K^{-1}	(G)-(G)	5	−175.846	1.0225	0.9974	0.1
	(L)-(L)	5	−136.511	1.0757	0.9972	0.1
	(L)-(G)	5	−213.903	1.0124	0.9857	1.0
	(Cr)-(Cr)	9	−87.153	0.8150	0.9946	0.1
$C_p^0(298)$, J mol^{-1}K^{-1}	(G)-(G)	4	14.263	0.7772	0.9982	1.0
Correlation pairs of type (II)						
$\Delta H_{form}^0(298)$, kJ mol^{-1}	(G)-(G)	5	52.413	1.0012	0.9980	0.1
	(G)-(L)	4	68.379	0.9262	0.9981	1.0
	(L)-(L)	4	54.241	0.9791	0.9995	0.1
$S^0(298)$, J mol^{-1}K^{-1}	(G)-(G)	4	−177.749	1.0294	0.9982	1.0
	(L)-(L)	5	−135.850	1.0702	0.9950	0.1
	(L)-(G)	4	−273.249	1.1546	0.9869	1.0
$C_p^0(298)$, J mol^{-1}K^{-1}	(G)-(G)	4	14.263	0.7772	0.9982	1.0

Remarks. The correlation of the properties for the physical states designated by (Φ_j) - (Φ_j) combines the variations of the properties in the pairs, in identical states, into a single linear variation; notation: N is the number of pairs, $\Delta\phi$ and β are parameters of Eqn.(8), r is the coefficient of the linear correlation of the properties, and α is the probable error of the correlation.
Note. G = gas, L = liquid, Cr = crystalline (Ed.of Translation).

According to the procedure proposed by Korshak and co-workers,[15] the choice of the polymers and the corresponding models in setting up a correlation series of properties ($\phi_{P,j}$ and $\phi_{M,j}$) must be made assuming an identical hypothetical process (conventional transition) for all the pairs,

relating, in conformity with Eqn.(8), the properties of the polymer unit $(-[-P-]_n-)$, the model $(R^1P_mR^2)$, and the compound R^1R^2:

$$R^1P_mR^2 \rightarrow \frac{m}{n}(-[-P-]_n-)+R^1R^2\ ; \quad m = 1, 2, \ldots, 4;\ n \rightarrow \infty\ . \tag{9}$$

According to this scheme, the polymer macromolecule can be obtained from the molecules of the model compound as a result of the abstraction of the elementary substituents and the formation of the molecules R^1R^2 from them. Compounds whose molecules undergo minimal chemical changes in reaction (9) can be usefully selected as models; in this sense R^1R^2 can be H_2, H_2O, HCl, etc. For example, the properties of vinyl polymers have been calculated[15,18] (Table 3) in conformity with conventional transitions of the type $HP_mH \rightarrow m-[-P-]- + H_2$ $(m = 1, 2)$, which permitted the use of correlation pairs of two types:

	Pair (I)	Pair (II)
Polymer (P)	$-CH_2-CHR-$	$-C(R^1R^2)-C(R^3R^4)-$
Model compound (M)	$H-[-CH_2-CHR-]_m-H$ $(m = 1, 2)$	$H-[-C(R^1R^2)-C(R^3R^4)-]_m-H$ $(m = 1)$

In order that calculations based on Eqn.(8) should yield the properties $\phi_{P,j}$ uncomplicated by the influence of the polymer end groups and hence referring to formation of the elementary polymer unit, it is necessary that the degree of polymerisation of the polymers involved in the correlation series should be fairly high. In those cases where it is difficult to select a model compound for the polymeric substance (for example, for a copolymer) corresponding to Scheme 9, it is possible to use a conventional transition with two model compounds R^1PR^2 and R^1SR^2, whose thermodynamic characteristics are known, i.e. a transition of the type

$$R^1PR^2 + R^1SR^2 \rightarrow \frac{1}{n}(-[-PS-]_n-) + 2R^1R^2, \tag{10}$$

where P and S correspond to the monomeric units of the copolymer.

2. Estimation of the Reliability of the Linear Correlation of the Parameters of the Model–Polymer Systems

We shall now consider the question of the reliability of the linear correlation method in relation to the correlation series of parameters for model–polymer systems in which the polymers belong to the vinyl series (Table 3). The constants of the correlation Eqn.(8), needed for the calculation of the thermodynamic parameters of the polymers, were found for three phase states of the latter: ideal gaseous, condensed (amorphous), and ideal crystalline. The coordinates of the reference points for their determination were the tabulated thermodynamic properties of model compounds[17] and certain reliable characteristics of the polymer systems obtained both experimentally (for the amorphous and amorphous-crystalline states of the systems—data from Ref.16#) and by calculation (for the ideal gaseous and crystalline states—data by Korshak and co-workers[15] and Marchenko[18] obtained by extrapolating the properties of oligomers to infinite molecular weight).

Statistical analysis of the correlation between the thermodynamic parameters of the vinyl polymers and models (Table 3) carried out using the Student t-statistic[15,18] showed that it is quite possible to describe this correlation by a linear regression equation with a probable error of the order of 0.1–1.0%. Furthermore, this analysis showed that the probable error can be reduced to $\alpha \leqslant 0.1\%$ (fiducial probability $P \geqslant 0.999$) in those cases where the most accurate thermodynamic parameters of the polymers and models are used as the coordinates of the reference points of the regression equation.

It should also be noted that, when there is a correspondence between the phase states of the vinyl polymers and model compounds, the correlation between their enthalpies of formation and entropies can be described on the basis of the constant difference principle, in conformity with which one puts $\beta = 1$ in Eqn.(8) with a probable error of 0.1–1.0%. The application of this method to calculations of the thermodynamic parameters of a series of polymers of practical importance has also been examined by Korshak and co-workers.[19]

The discrepancies between the results of the calculation in accordance with this scheme of the enthalpies of formation, entropies, and heat capacities of polymers and the experimental data, which exceed the probable error of the correlation by 1–5%, can arise, in particular, because the experimental data refer to polymer specimens which have been inadequately investigated from the standpoint of their physical state. More notable discrepancies can be a consequence of inaccuracies in the study of the chemical structures of the polymer specimens.

3. Methods for the Extrapolation of the Properties of Polymer-Analogue Model Compounds to Infinite Molecular Weight

We shall consider yet another version of the modelling method whereby it is possible to calculate effectively the standard thermodynamic parameters of polymers and which will be referred to as the method of extrapolation of the properties of polymer-homologues to infinite molecular weight.[18,19] Hitherto undeservedly little attention has been devoted to studies concerning the calculation of the thermodynamic parameters of polymeric substances. During the last 30 years, only about ten investigations have been reported[21–32] in which mainly the physical characteristics of amorphous polymers were estimated on the basis of the properties of n-paraffins and certain other simplest homologous series (in particular, the densities, surface tensions, cohesion energies, dielectric constants, etc. have been determined) and only a few communications[28–30] have been devoted to the estimation of the thermodynamic parameters of liquid and gaseous paraffinic hydrocarbons with infinitely long chains both unbranched and branched [branches of the type of $-CH(CH_3)-$ and $-C(CH_3)_2-$ at each third, fourth, and fifth carbon atom in the chain]. For example, the heat of formation (per $-CH_2-$ group) of an infinite polymethylene chain in the gaseous state has been found by this method[28] as −20.61 kJ mol^{-1}. The entropy increment per $-CH_2-$ group has been calculated for the same polymer by an analogous procedure[29] as 38.95 J mol^{-1} K^{-1}.

The method of calculation of the thermodynamic properties of polymers considered here is based on the concept of polymeric substances as the limiting members of the corresponding polymer-analogue series of substances; the possibility of estimating these properties by extrapolating the specific characteristics of the members of the polymer-analogue series to infinite molecular weight follows directly from this concept. The application of the method indicated requires the knowledge of the characteristic features of the changes in the thermodynamic properties in the polymer-analogue series of substances, starting with the lowest members of the series, normally employed as models of polymers, and ending with the highest limiting members of the series, whose mixture constitutes in effect real polydisperse polymers. If one begins with the hypothesis that

There is no reference 16 in the Russian text (Ed.of Translation).

the contributions to the parameters of the repeating structural units and the end groups are additive for the highest members of the series, while only small deviations from additivity are characteristic of the lowest members, then a thermodynamic property of the molecule Φ_n, corresponding to the nth member of the series with a molecular weight M_n, can be represented in the following form:

$$\Phi_n = \sum_{i=1}^{n+2} m_i\varphi_i + \delta_n = m_1\varphi_1 + m_2\varphi_2 + nm_0\varphi_0 + \delta_n , \qquad (11)$$

where ϕ_0 denotes the specific contribution to the property Φ_n of the repeating structural element of a chain with a mass m_0, ϕ_1 and ϕ_2 are the specific contributions to the property Φ_n by the two end groups with masses m_1 and m_2 respectively, and δ_n is a small correction which becomes a maximum for $n = 0$ (this value characterises the end groups of molecules of the given series) and becomes zero for the highest members of this series, i.e. $\lim_{n\to\infty} \delta_n = 0$.

The nature of the correction δ_n is such that it defines the change in the intensity of the non-valence intramolecular and intermolecular interactions of the atoms and the deformations of the valence angles in the sequence of molecules constituting the given polymer-analogue series. It is quite understandable that it must be taken into account in determining the exact dependence of the thermodynamic properties of the members of the series on the molecular weight. In a study of the variation of the enthalpies of formation of the lowest members of the homologous series of hydrocarbons in the gaseous state, Prosen et al.[32] established that δ_n can be neglected not at $n = \infty$ but much earlier when the number of repeating CH_2 groups in the hydrocarbon corresponds to $n \geq 4$. Thus, starting with $n_0 = 4$, the quantity δ_n becomes zero regardless of the nature of the end groups of the hydrocarbons. For other, longer repeating structural units, for example such as $-C_6H_4-$, $-C_6H_4O-$, $-C_6H_4NHCO-$, etc., we have $n_0 < 4$.

Thus if members corresponding to $n < n_0$ are removed from the homologous series of compounds, then the properties of the remaining members can be described with the aid of only the linear part of Eqn.(11).

In order to characterise the properties of members of a polymer-analogue series, it is useful to introduce two constants which are independent of the molecular weight of the members of the given series:

$$k_\varphi = (m_1\varphi_1 + m_2\varphi_2)/m_0\varphi_0; \quad k_m = (m_1 + m_2)/m_0 . \qquad (12)$$

On the basis of Eqns.(11) and (12), it is possible to calculate the required specific contributions to the property Φ_n of the repeating structural element of the polymer in the following manner:

$$\varphi_0 = (\Phi_n - \delta_n)/(k_\varphi + n)m_0 . \qquad (13)$$

It is noteworthy that the magnitude of this contribution should not in principle depend on the form of the end groups of the molecules of the polymer-analogue series, which are in the gaseous state or in a condensed phase. On the other hand, the specific value of the given property ϕ_n determined directly from the experimental results contains in all cases a contribution by the end groups of the molecule of the nth member of the series, which depends on n, since the expression

$$\varphi_n = \Phi_n/M_n = \Phi_n/(k_m + n)m_0 , \qquad (14)$$

corresponds to it. It follows from a comparison of Eqns.(13) and (14) that

$$\varphi_n = \varphi_0[1 + (k_\varphi - k_m)/(k_m + n)] + \delta_n/M_n \qquad (15)$$

where δ_n/M_n corresponds to the specific deviation of the property from additivity.

If one confines oneself in the treatment of a polymer-analogue series only to its terms ($n \geq n_0$) for which one can neglect the ratio δ_n/M_n, then Eqn.(15) assumes a form convenient for the calculation of ϕ_0:

$$\varphi_n = \varphi_0[1 + (k_\varphi - k_m)/(k_m + n)] . \qquad (16)$$

As can be seen from Eqns.(15) and (16), by extrapolating ϕ_n to $1/(k_m + n) = 0$, it is easy to obtain the increment of the thermodynamic parameter of the polymer ϕ_0. Furthermore, on the basis of Eqn.(16), it is convenient to estimate the limiting molecular weight of the chains, at and above which the difference between ϕ_n and ϕ_0 should be neglected. Since Eqn.(16) is a fractional-linear function of n, for which $\phi_n/\phi_0 = 1$ is one of the asymptotic forms, the specific property ϕ_n obtained directly from the experimental results can be assumed equal to ϕ_0 only for fairly large values of $n \to \infty$.

When determining the constant parameters k_ϕ and ϕ_0, one can employ, together with Eqns.(15) and (16), simple relations which use the known values of the properties of only two members of the series, for example Φ_n for the nth member and Φ_r for the rth member ($n > r$):

$$k_\varphi = (n\Phi_r - r\Phi_n)/(\Phi_n - \Phi_r); \quad \varphi_0 = (\Phi_n - \Phi_r)/(n - r)m_0 . \qquad (17)$$

As stated above, the choice of the given members of the series is limited to the group of substances for which r is greater than a limiting values n_0, starting from which the change of the properties in the series involves a regular increment in $\phi_0(\delta_{n_0} = 0)$.

Since the choice of members of the polymer-analogue series with $n \geq n_0$ for different chain lengths has a negligble influence on the parameters k_ϕ and ϕ_0 found from Eqn.(16), it is logical to suppose that their values do not change also in the case of a polydisperse mixture made up of molecules of the same series. In this case it is clear that the ratio of the properties $\bar{\phi}_n$ and ϕ_0 in the nth fraction of the polydisperse polymer, characterised by the number-average quantities $\bar{\Phi}_n$ and degree of polymerisation $\bar{n}$, can be obtained with the aid of an expression analogous to Eqn.(16):

$$\bar{\varphi}_n/\varphi_0 = 1 + (k_\varphi - k_m)/(k_m + \bar{n}) , \qquad (18)$$

where $\bar{\Phi}_n = \phi_0$ only when $\bar{n} \to \infty$. When $\bar{n} = 10^3$ and $k_\phi - k_m = 1$, the approximation $\bar{\phi}_n = \phi_0$ leads to an error of 0.1% in the determination of ϕ_0 and of 10% in the molar quantity for $m_0 = 100$.

It is noteworthy that the character of the variation of the thermodynamic properties of polymeric substances as a function of $\bar{n}$, expressed by Eqn.(18), is general. In particular, it can be shown that the polymerisation equilibrium constants corresponding to the stages involving the interaction of the monomer with the initiator (K_1) and its dimerisation (K_2), trimerisation (K_3), etc. obey analogous relations. The variation of the equilibrium constants in the sequence K_1, K_2, ..., K_n characterises primarily the variation of the thermodynamic properties of compounds in a polymer-analogue series corresponding to this sequence. In the polymerisation of a monomer M in the presence of an initiator XY

$$XY + M \overset{K_1}{\rightleftarrows} XMY,\ XMY + M \overset{K_2}{\rightleftarrows} XM_2Y, \ldots,\ XM_{n-1}Y + M \overset{K_n}{\rightleftarrows} XM_nY$$

which is frequently encountered in practice, the Tobolsky approximation[33] $K_1 \neq K_2$, $K_2 = K_3 = \ldots = K_n = \ldots = K$ holds with adequate accuracy. From it, it is easy to obtain an equation relating the equilibrium constant K to the number-average degree of polymerisation of the polymer chains:

$$K = \frac{1}{[M]}\left[1 - 1/(\bar{n} - 1)\right] , \qquad (19)$$

where [M] is the equilibrium concentration of the monomer. Subject to the condition that $\bar{n} \to \infty$, we have $K_\infty = 1/[M]$ and consequently

$$K = K_\infty[1 - 1/(\bar{n} - 1)]. \quad (20)$$

It can be seen that the character of relations (18) and (20) is the same although, compared with Eqn.(20), the initial significance of the constants k_ϕ and k_m, inherent in Eqn.(18), is clearly different. In this case Eqn.(20) shows that, when the Tobolsky approximation is valid, the true value of the equilibrium constant of the n-merisation stage is smaller than the limiting equilibrium constant K_∞ (corresponding to the formation of infinitely long chains) by an amount inversely proportional to the number-average degree of polymerisation of the product.

Another example, confirming the general character of the variation of the thermodynamic properties in a polymer-analogue series, expressed by Eqn.(18), is the analogous dependence of the enthalpy of polymerisation of the monomer on the number-average degree of polymerisation. For example, in the case of α-methylstyrene, this relation has the following form:[34]

$$\Delta H^0_{pol}(298)\ (\text{kJ mol}^{-1}) = 34.74\ (1 + 2.205/\bar{n}). \quad (21)$$

It is possible to quote a much greater number of similar examples. However, here it is more important to note that in all such cases, where the limiting parameter ϕ_0 is found by extrapolating function (18) to the limit $1/(k_m + \bar{n}) = 0$, it is necessary to make preliminary experimental determinations of the number-average values of the property $\bar{\phi}_n$ and degree of polymerisation $\bar{n}$ for several fractions of the polymer. These are extremely laborious and at the same time need to be fairly accurate.

Thus, in order to obtain fundamental thermodynamic characteristics of the polymers such as ϕ_0, which are independent of the average molecular weight and the molecular weight distribution of the polymer macromolecules, one can employ, on the one hand, the version of the modelling method examined above and the corresponding Eqns.(15) and (16) and, on the other hand, one can carry out a direct experimental study of the properties of different fractions of the polymer itself and then calculate ϕ_0 from Eqn.(18). Although the second procedure is now more commonly used in practice, the results obtained by this method as a rule require confirmation and refinement, since for most of them it is impossible to find corrections for the different phase states of the polymer and to allow for the presence of chemical cross-links and chain branches as well as contaminations associated with the employment of initiators, catalysts, emulsifying agents, etc. in the polymerisation process. On the other hand, extrapolation of the properties of the individual models of compounds to $n \to \infty$ in accordance with Eqn.(16), which is used in the first procedure, does not require a complex allowance for corrections associated with the specific features of the synthesis of the polymer and, what is particularly important, this method makes it possible to determine with satisfactory accuracy the properties of polymer chains in three ideal states of aggregation: in the solid (crystalline), liquid, and ideal gas states (Table 4). With the aid of extrapolation, it is then possible to proceed from ideal characteristics to the thermodynamic properties of a real amorphous-crystalline polymer, in the case where the degree of crystallinity of the polymer is known. For example, the enthalpy of formation of a 100% crystalline polymer can be extrapolated to the real degree of crystallinity w on the assumption that the difference between the enthalpies of formation of the polymer for degrees of crystallinity of 0% and w% is proportional to the degree of crystallinity:

$$\Delta H^0_{form}(298;\ w) = \Delta H^0_{form}(298;0\%) - w\,[\Delta H^0_{form}(298;0\%) - \Delta H^0_{form}(298;100\%)].$$

Finally, it is quite possible to infer the energy of formation of the real crystal lattice of the polymer from the difference between the enthalpies of formation of the polymer in the ideal gaseous and crystalline states.[30]

Table 4. Dependence of the specific thermodynamic properties of compounds in homologous series on the molecular weight.[18]

Compound	n	State	φ_0	$(k_\varphi - k_m)\varphi_0$	r
			$\varphi = \Delta H^0_{form}$ (298), kJ g^{-1}		
$H(CH_2)_{2n}H$	2—12	G	−1.469	−1.452	−0.9972
»	2—10	L	−1.827	−1.477	−0.9981
»	5—12	Cr	−2.404	−1.114	−0.9932
$H(CH_2)_{2n+1}H$	2—8	G	−1.472	−1.395	−0.9982
»	2—8	L	−1.815	−1.532	−0.9980
»	5—12	Cr	−2.093	−0.720	−0.9937
$H(CH_2)_nH$	2—20	G	−1.469	−2.906	−0.9991
»	4—20	L	−1.825	−2.962	−0.9988
»	10—24	Cr	−2.400	−1.869	−0.9600
			$\varphi = S^0$ (298), J g^{-1}K^{-1}		
$H(CH_2)_{2n}H$	2—40	G	2.782	5.299	0.9998
»	2—40	L	2.290	3.794	0.9625
»	10—16	Cr	1.737	2.361	0.9783
$H(CH_2)_{2n+1}H$	2—9	G	2.789	5.275	0.9998
»	2—9	L	2.300	3.524	0.9994
$H(CH_2)_nH$	4—20	G	2.782	10.599	0.9960
»	4—20	L	2.319	6.843	0.9988
			$\varphi = C^0_p$ (298), J g^{-1}K^{-1}		
$CN(CH_2)_{2n}H$	1—6	G	2.776	4.634	0.9999
$H(CH_2)_{2n}H$	1—40	G	1.623	1.292	0.9732
$H(CH_2)_nH$	1—19	G	1.630	1.900	0.9950
$CN(CH_2)_{2n}H$	1—6	G	1.640	−0.643	−0.9995
$CN(CH_2)_{2n+1}H$	1—5	G	1.620	−0.565	−0.9993

Remarks. ϕ_0 and $(k_\phi - k_m)\phi_0$ are parameters of correlation (16), r is the coefficient of the linear correlation, and α is the error of the correlation, equal in all cases to 0.1%.
Note. G = gas, L = liquid, Cr = crystalline (Ed.of Translation).

A useful consequence of Eqn.(16) is the possibility of employing the relation between two different properties ψ_n and ϕ_n of compounds of the same polymer-analogue series (for compounds of two different series characterised by the same values of k_m and n) in the form

$$\psi_n = A + B\varphi_n, \quad (22)$$

where $A = \psi_0(k_\phi - k_\psi)/(k_m - k_\phi)$ and $B = \psi_0(k_\psi - k_m)/\phi_0(k_\phi - k_m)$. The constants used to determine A and B have the same significance as in Eqn.(16).

Thus relations similar to Eqn.(22) can also be used to extend the range of data both on the compounds of polymer-analogue series and the polymers themselves.

4. The Reliability of the Extrapolation Method

In order to estimate the reliability of the calculations by the method involving the extrapolation of the thermodynamic parameters of polymers in the ideal gaseous and condensed states, Eqn.(16) has been applied[18] to thoroughly investigated homologous series of compounds of the type $R^1(CH_2)_nR^2$

(R^1, R^2 = H, H, or CN, H).[17] For this purpose, the thermodynamic parameters of compounds of the corresponding series [$\Delta H^0_{form}(298)$, $S^0(298)$, and $C^0_p(298)$] were treated as functions of $1/(k_m + n)$ alternately for three ideal physical states—gaseous, liquid, and crystalline. Table 4 shows that the above relations can be fitted by linear functions of $1/(k_m + n)$ of the type of Eqn.(16) with a high degree of reliability. This is indicated, in particular, by the closeness of the coefficients of linear correlation obtained to unity. Furthermore, statistical analysis of the relations using the Student t-statistic showed that a linear correlation of type (16) holds with a fiducial probability $P \geq 0.999$ for the given homologous series (the error of the correlation $\alpha \leq 0.1\%$).

Extrapolation of the specific values of the thermodynamic functions of n-paraffins to $1/(k_m + n) = 0$ yields the enthalpies of formation and entropies of polyethylene corresponding to three phase states of its macromolecules: ideal gaseous, liquid, and crystalline. Table 4 shows that the results of this extrapolation in the series of even and odd n-paraffins differ somewhat. The difference, for example for the increment of the enthalpy of formation per $-CH_2-$ group in the crystalline state is 0.6%, which exceeds severalfold the experimental error of the given characteristic for n-paraffins (~0.1%). The appearance of this effect may be attributed to different symmetries of the even and odd molecules. The studies by Muller and Lonsdale,[35] Schaerer et al.[36], and Piper[37] showed that the alternation of the melting points between the even and odd n-paraffins (the melting point is higher for the even members) is due to the alternation of two different types of their crystal structure: the orthorhombic modification of the short odd members of the series alternates with the triclinic modification of the even members having $n_C \leq 28$. On the basis of the results of these studies, one can assume that the extrapolation of the thermodynamic properties of crystalline n-paraffins with an even number of carbon atoms ($4 \leq 2n_C \leq 28$, Table 4) to the region of infinite molecular weights yields the properties of the triclinic crystalline modification of polyethylene. An analogous operation for n-paraffins with an odd number of carbon atoms makes it possible to estimate the thermodynamic characteristics of the orthorhombic crystalline modification of polyethylene, which is the commonest type of the unit cell for this polymer.[38]

The results obtained by Marchenko[18] agree with other data.[16,28,29] In particular, the increments in the enthalpy of formation and entropy per $-CH_2-$ group for the gaseous state of the chains of this polymer, listed in Table 4 [$\Delta H^0_{form}(298, \text{gas}) = -1.469 \times 14.027 = -20.602$ kJ mol^{-1} and $S^0(298, \text{gas}) = 2.782 \times 14.027 = 39.02$ J mol^{-1} K^{-1}] are consistent with the enthalpy of -20.61 kJ mol^{-1} and the entropy of 38.93 J mol^{-1} K^{-1} from other studies.[28,29] Furthermore, linear interpolation of the increments of the enthalpy of formation of the fully crystalline state [$\Delta H^0_{form}(298, \text{cryst.}) = -2.093 \times 14.027 = -29.36$ kJ mol^{-1}] and the fully amorphous state [$\Delta H^0_{form}(298, \text{amorph.}) = -1.815 \times 14.027 = -25.46$ kJ mol^{-1}] yields the enthalpy of formation (-28.19 kJ mol^{-1}) for the real amorphous-crystalline state of polyethylene with a degree of crystallinity of ~70%,[39] which agrees well with the experimental value (-28.03 kJ mol^{-1}).[16]

5. The Difference Interpolation Method

The possibility of applying the relations of difference interpolation to calculations of the physicochemical properties of polymers has been pointed out in a number of studies.[18,19,40] According to the difference interpolation method, a thermodynamic property ϕ, which depends on different sets of structural elements m_1, m_2, ..., m_n, can be represented in the form

$$\varphi(m_1, m_2, \ldots, m_n) = \varphi(0, 0, \ldots, 0) + \sum_k C^{\lambda_{m_1}}_{m_1} C^{\lambda_{m_2}}_{m_2} \ldots C^{\lambda_{m_n}}_{m_n} \Delta^{k-\lambda_1+\lambda_2+\ldots+\lambda_n}_{\lambda_{m_1}\lambda_{m_2}\ldots\lambda_{m_n}} \varphi(0, 0, \ldots, 0) \quad , \tag{23}$$

where $\phi(0, 0, \ldots, 0)$ is the value of the function ϕ for standard values of the discrete variables m^0_1, m^0_2, ..., m^0_n, $\Delta^k_{\lambda_{m_1}\lambda_{m_2}\ldots\lambda_{m_n}} = \lambda_1 + \lambda_2 + \ldots + \lambda_n \phi(0, 0, \ldots, 0)$ are finite differences, and $C^{\lambda_{m_1}}_{m_1}$, $C^{\lambda_{m_2}}_{m_2}$, ..., $C^{\lambda_{m_n}}_{m_n}$ are the numbers of the corresponding combinations.

Eqn.(23) is extremely cumbersome, but its application to calculations on polymers is facilitated by the fact that many macromolcules are linear sequences of isotypical atomic groups. As shown above, the properties of such polymers, starting from a fairly large average mass, cease to depend on the chain length, i.e. for certain average chain lengths the contribution of the end groups to the properties of the polymer is no longer appreciable. The thermodynamic properties of the polymer are in this case a function of the number and type of atoms or groups of atoms constituting the elementary structural chain units.

As an example, Pavlinov et al.[40] examined the vinyl series of polymers. An individual polymer chain of this series was represented in the form $-[-CH_{2-m_1}X_{m_1} - CH_{2-m_2}X_{m_2}-]-$, where X is a univalent substituent (X = H, Cl, CH_3, C_6H_5, etc.) and m_1 and m_2 are the numbers of substituents in the elementary unit (m_1, m_2 = 0, 1, 2; $m_1 \leq m_2$). In this case the properties of the polymer, referred to the elementary unit, are a function of only the two variables m_1 and m_2. Then, approximating to within second order differences, we have

$$\varphi(m_1, m_2) = \varphi(0, 0) + (m_1 + m_2)\,\Delta^1_{1,0}\varphi(0, 0) + \frac{1}{2}[m_1(m_1 - 1) + m_2(m_2 - 1)]\,\Delta^2_{2,0}\varphi(0, 0) + m_1 m_2 \Delta^2_{1,1}\varphi(0, 0) \, . \tag{24}$$

Here the point (0, 0) corresponds to unsubstituted polyethylene and finite differences of the type

$$\begin{aligned} \Delta^1_{1,0}\varphi(0, 0) &= \Delta^1_{0,1}\varphi(0, 0) = \varphi(1, 0) - \varphi(0, 0) \, , \\ \Delta^2_{1,1}\varphi(0, 0) &= \varphi(1, 1) - 2\varphi(1, 0) + \varphi(0, 0) \, , \\ \Delta^2_{2,0}\varphi(0, 0) &= \Delta^2_{0,2}\varphi(0, 0) = \varphi(2, 0) - 2\varphi(1, 0) + \varphi(0, 0) \end{aligned} \tag{25}$$

correspond to different degrees of X-substitution of the polymer unit. It is more convenient to use Eqn.(24) in the form

$$\varphi(m_1, m_2) = \varphi_0 + (m_1 + m_2)\varphi_1 + (m_1 + m_2)^2\varphi_2 + m_1 m_2 \varphi_3 \, , \tag{26}$$

where ϕ_0, ϕ_1, ϕ_2, and ϕ_3 are linear combinations of $\phi(0, 0)$, $\Delta^1_{1,0}\phi(0, 0)$, $\Delta^2_{1,0}\phi(0, 0)$, and $\Delta^2_{1,1}\phi(0, 0)$ of the type $\phi_0 = \phi(0, 0)$, $\phi_1 = \Delta^1_{1,0}\phi(0, 0) - \frac{1}{2}\Delta^2_{2,0}\phi(0, 0)$, $\phi_2 = \frac{1}{2}\Delta^2_{2,0}\phi(0, 0)$ and $\phi_3 = \Delta^2_{1,1}\phi(0, 0) - \Delta^2_{2,0}\phi(0, 0)$ characterising only the form of the substituent X.

If the order of the substitution in the formation of disubstituted polyethylene is immaterial, i.e. if $\Delta^2_{1,1}\phi(0, 0) = \Delta^2_{2,0}\phi(0, 0)$, then $\phi(m_1, m_2)$ can be represented in the form of a parabolic function of the total substitution number $l = m_1 + m_2$:

$$\varphi(m_1, m_2) = \varphi_0 + \varphi_1 l + \varphi_2 l^2 \tag{27}$$

In terms of their structure, Eqns.(24), (26), and (27) reflect the pair-additive approach of Bernstein.[1] With certain simplifications, it is easy to obtain on the basis of Eqns. (24), (26), and (27) a series of semiempirical schemes for

the calculation of the physicochemical properties of substances.[13,14,41–43]

Table 5. The results[40] representing in the form of the function $\phi(m_1, m_2) = \phi_0 + \phi_1 l + \phi_2 l^2$ the thermodynamic and kinetic experimental data[16,43,46,52] characterising X-substituted derivatives of polyethylene, their thermal decomposition processes, and the polmerisation of X-derivatives of ethylene.

φ	X	State	φ_0	φ_1	φ_2
ΔH^0_{form} (298), kJ mol^{-1}	Cl	S	−58.6*	−26.4*	1.7*
	Cl	G	−41.0	−26.8	−3.8
	F	S	−54.4*	−227.6*	9.6*
	F	G	−41.0	−187.0	0
	CH_3	S	−56.1	−38.9	11.3
		G	−41.0	−23.0	−3.8
S^0 (298), J mol^{-1}K^{-1}	Cl	S	47.7	15.5	2.1
	F	S	48.1	2.9	3.3
	CH_3	S	48.1	38.5	−7.1
C_p^0 (298), J mol^{-1}K^{-1}	Cl	S	49.0	5.4	5.9
	CH_3	S	49.0	51.9	−10.9
ΔH^0_{pol} (298), kJ mol^{-1}	Cl	L, S	−88.7	−20.9	13.8
	F	L, S	−88.7	−24.3	2.1
	CH_3	L, S	−88.7	−2.9	10.0
ΔS^0_{pol} (298), J mol^{-1}K^{-1}	Cl	G, S	−173.6	−0.8	−6.7
	Cl	L, S	−100.4	−17.8	5.2
	CH_3	G, S	−173.6	−15.9	2.1
$E_a^{\neq}$, kJ mol^{-1}	F	S, G	265.3*	−87.9*	25.9*
	CH_3	S, G	263.6	−12.6	−8.4
T_{hd}, °C	F	S, G	411.5*	−52.3*	18.8*
	CH_3	S, G	406.0	−9.0	−10.0

*The results have been obtained[40] by solving a system of three linear equations.
Note. G = gas, L = liquid, and S = solid (Ed.of Translation).

As a consequence of the insufficiency of literature data (see the relevant reviews[16,31,39,43–46]), thermodynamic characteristics of F-, Cl-, and CH_3-substituted polyethylene derivatives such as the enthalpy of formation, the entropy, and the heat capacity have been estimated[40] within the framework of the approximation defined by Eqn.(27). The constants ϕ_0, ϕ_1, and ϕ_2 required for the calculation (Table 5) were obtained in two ways. The first way consisted in solving a system of three linear algebraic equations using the known values of the thermodynamic parameter for all three X-substituted polyethylene derivatives (with $l = 0, 1, 2$, or $l = 0, 2, 3$). In this case the non-averaged constants ϕ_0, ϕ_1, and ϕ_2 were used to calculate the properties of the polymers; the calculations of $\phi(m_1, m_2)$ then fully reproduced the reference data despite the possibility of the inaccuracy of the former (see Table 6). In those cases where the number of equations exceeded the number of unknown constants (one property was investigated by different workers), the system was solved by the method of least squares, which yielded more accurate (average) coefficients ϕ_0, ϕ_1, and ϕ_2. Extrapolation of function (27) ("forward" and "backwards") made it possible to obtain the hitherto uninvestigated properties for two other degrees of substitution of the polymer ($l = 3$, 4 or $l = 1$, 4; Table 6).

Comparison of the difference terms ϕ_0, ϕ_1, and ϕ_2 (Table 5), found from the enthalpies of formation of F-, Cl-, and CH_3-substituted polyethylenes, corresponding repsectively to the condensed phase and the state of isolated chains shows that the transition of the polymer from the first physical state to the second alters most the quadratic term in the approximation equation (27). Relations of type (27) for the enthalpies of formation of F-substituted polyethylenes (in the gaseous state) and the entropies of Cl-substituted polyethylenes (in the solid state) and also for the enthalpies and entropies of

Table 6. Comparison with experimental data of the thermodynamic and kinetic quantities calculated[40] in terms of the quadratic approximation and characterising X-substituted polyethylenes, their thermal decomposition processes, and the polymerisation of X-substituted derivatives of ethylene.

l	$-\Delta H^0_{form}$ (298; S), kJ mol^{-1}		S^0 (298; S), J mol^{-1}K^{-1}		$-\Delta H^0_{pol}$ (298; L, S), kJ mol^{-1}		$-\Delta S^0_{pol}$ (298; G, S), J mol^{-1}K^{-1}		$-\Delta S^0_{pol}$ (298; L, S), J mol^{-1}K^{-1}		$E_a^{\neq}$ (S, G), kJ mol^{-1}		T_{hd}, °C (S, G)	
	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.	expt.	calc.	(Ref.52)	calc.	(Ref.52)
						X = CH_3								
0	56.1	56.1 [53—55]	48.1	48.1 [46, 48]	88.7	87.7 [53]	173.6	173.6 [49]	100.4	100.4 [16]	264	264	406	406
1	83.7	83.7 [56]	79.5	79.5 [49]	81.6	81.6 [79]	187.4	187.4 [46]	116.3	116.3 [6]	243	243	387	387
2*	88.7	88.7 [55]	96.7	96.7 [50]	54.0	54.0 [80]	197.1	197.1 [46]	120.5	120.5 [6]	205	205	348	348
3	71.1	—	95.4	—	−5.9	—	202.5	—	113.0	—	151	—	289	—
4	31.0	—	88.3	—	−62.8	—	203.6	—	93.7	—	79	—	21	—
						X = Cl								
0	58.6	56.1 [53—55]	47.7	48.1 [46, 48]	88.7	88.7 [53]	173.6	173.6 [49]	100.4	100.4 [16]	—	—	—	—
1	83.7	81.2 [45, 47] 94.6 [61]	65.3	65.3 [46]	95.8	95.8 [61]	181.2	181.2 [46]	113.0	113.0 [46]	—	—	—	—
2*	104.6	100.4 [61]	83.7	87.0 [46]	75.3	75.3 [61]	202.5	202.5 [46]	115.0	115.1 [46]	—	—	—	—
3	121.8	—	110.5	—	27.2	—	237.7	—	106.7	—	—	—	—	—
4	135.6	—	146.0	—	−48.5	—	286.6	—	87.9	—	—	—	—	—
						X = F								
0	54.4	56.1 [53—55]	48.1	48.1 [46, 48]	88.7	88.7 [53]	—	173.6 [49]	—	100.4 [16]	264	264	411	406
1	272.4	267.8**	54.4	54.4**	111.3	—	—	—	—	—	205	—	378	389
2*	471.1	474.0 [62]	67.4	—	128.9	128.9 [62]	—	—	—	—	192	205	382	—
3	650.6	651.0**	87.0	—	144.3	—	—	—	—	—	234	222	423	413
4	810.9	809.6 [4]	113.4	113.4 [51]	154.8	154.8 [63]	—	197.1 [6]	—	118.1 [81]	331	335	503	509

*1,1-Disubstituted ethylene.
**Results obtained by Pavlinov et al.[40] using the method of linear correlations.
Note. G = gas, L = liquid, and S = solid [numbers in square brackets denote references (Ed.of Translation)].

polymerisation of F- and CH_3-derivatives of ethylene, corresponding to transitions of the type (liq.) → (solid) and (gas) → (solid), differ little from the linear relation, in contrast to the others examined in Table 5. Eqn.(27) can be linear only subject to the condition that $\Delta^2_{1,1}\phi(0, 0) = \Delta^2_{2,0}\phi(0, 0) = 0$. In this case there is a simple additive relation between the property and the degree of substitution:

$$\varphi(m_1, m_2) = \varphi_0 + \varphi_1 l. \qquad (28)$$

An analogous form of approximation has been used, for example, in Szabo's method of increments for C–C bonds.[41]

In this case, on comparing the properties of a series of derivatives of polyethylene with two types of substitution, namely $-[-CH_{2-}m_1\text{-}n_1X_{m_1}Y_{n_1}\text{-}CH_{2-}m_2\text{-}n_2X_{m_2}Y_{n_2}-]-$ (A) and $-[-CH_{2-}m_1X_{m_1}\text{-}CH_{2-}m_2X_{m_2}-]-$ (B), for which the variable factor is only the type of substituent X while the substitution numbers m_1, m_2, n_1, and n_2 and the type of substituent Y are fixed, it is possible to put forward, on the basis of Eqn.(27), a simple relation between the properties of the corresponding members of these series:

$$\varphi_A(X) = \Delta\varphi^0_{A,B} + \varphi_B(X), \qquad (29)$$

because

$$\Delta\varphi^0_{A,B} = \varphi_A(0) - \varphi_B(0) + (\varphi^A_{1,A} - \varphi_{1,B})\,l + (\varphi_{2,A} - \varphi_{2,B})\,l^2 + m_1m_2(\varphi_{3,A} - \varphi_{2,B}) = \text{const}.$$

Eqn.(29) reproduces the rule of constant differences for the properties of isotypical substances formulated by Karapet'yants.[13] Its applicability to vinyl polymers has been confirmed[40] with the aid of pair-correlation analysis.[20] Examination of the relations between the thermodynamic parameters [$\Delta H^0_{form}(298)$ and $S^0(298)$] of two groups of vinyl polymers of the type $-[-CH_2-C(CH_3)X-]-$ and $-[-CH_2-CHX-]-$ with different substituents X (H, CH_3, COOH, $COOCH_3$, and C_6H_5) showed[40] that they are linear with a fiducial probability $P \geq 0.999$ and a probable correlation error $\alpha \leq 0.1\%$. Their linear correlation coefficients are in the range 0.98–0.99. Relations of this kind also make it possible in many instances to estimate thermodynamic parameters where experimental data either do not exist or are difficult to determine.

The application of the interpolation method when the dependence of the thermodynamic and kinetic parameters of polymerisation reactions of the ethylene derivatives $CH_{2-}m_1X_{m_1} = CH_{2-}m_2X_{m_2}$ on the number or type of substituents X is considered merits particular attention. In relation to polymerisation reactions, Eqns.(26) and (27) can be written in an analogous form for both thermodynamic and kinetic reaction parameters, since the number and type of substituents per mole of the monomer which has reacted or been activated do not change in this process.

The parabolic function (27) describes fairly adequately the dependence of the enthalpies and entropies of polymerisation of F-, Cl-, and CH_3-substituted ethylenes on the number l (Table 6). On the basis of the relations $\Delta H^0_{pol} = f(l)$ and $\Delta S^0_{pol} = \phi(l)$ obtained in this way (Table 6), it has been shown[40] that the polymerisation of ethylene derivatives containing three (and, even more so, four) substituents of the type of Cl and CH_3 is thermodynamically unfavourable even at room temperature (298 K), since $\Delta G^0_{pol} = \Delta H^0_{pol} - 298\Delta S^0_{pol} > 0$. At higher temperatures the thermodynamic prohibition of the polymerisation of these systems becomes even more stringent. Judging from the available experimental data (see the relvant reviews[16,46]) and the data in Table 6, the polymerisation of F-substituted ethylenes is thermodynamically allowed for all degrees of substitution of ethylene, because different values of l (1, 2, 3, 4) give high negative values of ΔG^0_{pol}.

The attempt to use the method of finite differences for a quantitative description of the kinetic parameters of a process as complex as the thermal decomposition of compounds of the vinyl series, involving the rupture of the principal bonds, is also of interest.[44,52] The activation energies $E^{\neq}_a$ and half-decomposition temperatures T_{hd} of a series of F- and CH_3-substituted polyethylenes[52] are described by the parabolic function (27) (Table 6) to within several per cent, which corresponds to the experimental error in the determination of these quantities. The parallel variation of $E^{\neq}_a$ and T_{hd} as a function of l in the case of the same substituent can be seen from Tables 5 and 6. The character of the variation of the thermal stability of the polymers with increase of l observed under these conditions in the main confirms the conclusions reached in a study[40] of the thermodynamics of the polymerisation of F- and CH_3-substituted ethylenes.

Thus the difference interpolation method yields a fully correct idea about the character of the changes in the properties of the simplest polymer systems as a function of the number and type of side substituents in the chain.

6. Thermodynamic Properties of Polyheteroarylenes

The modelling methods described above can be successfully employed to calculate the thermodynamic parameters not only of polymers with a simple chemical structure but also of complex systems such as polyheteroarylenes.[19] The attempts at an exact determination of the heats of formation of these polycondensation polymers directly with the aid of combustion calorimetry as a rule encounter serious difficulties.[82–88] On the other hand, the application of reaction calorimetry also does not always achieve this aim[18,19] as a consequence of the complexity of the synthesis of the above systems (sometimes involving a multistage process). By virtue of the competition between the main polycondensation reaction of the starting materials with various secondary reaction pathways, many of the rigid-chain polyheteroarylenes have a "heterounit" structure of the macromolecules, i.e. contain an appreciable amount of chemically defective structural fragments.[19,89,90] For example, in the two-stage synthesis of polyheteroarylenes, where polyfunctional amines and dianhydrides (dichlorides) of aromatic di- or tetra-carboxylic acids are used as the starting materials, the final polycondensation products are usually infusible and insoluble substances containing complex combinations of the fragments of the initial, intermediate, and final polymeric structures.[89,90] For this reason, the experimental thermodynamic characteristics of polyheteroarylenes usually require more fundamental checks with the aid of phenomenological computational methods than the analogous characteristics of other less complex polymers.

The thermodynamic properties of polyheteroarylenes have now been calculated so far in only one study[19] with the aid of the method based on the linear correlation of properties in model–polymer systems (Table 7). In the determination of the enthalpies of formation of polyheteroarylenes in the above investigation, the simplest version of the correlation method, namely the rule of constant differences between the properties of isotypical polymers (P_i) and model substances (M_i), was employed. In conformity with this rule, it was assumed that $\beta = 1$ and $\Delta(\Delta H^0_{form}) = \text{const}$. (corresponds to a constant increment in the end groups R^1 and R^2 of the models M_i) in the expression

$$\Delta H^0_{form}(298, P_i) = \Delta(\Delta H^0_{form}) + \beta \cdot \Delta H^0_{form}(298, M_i) \qquad (30)$$

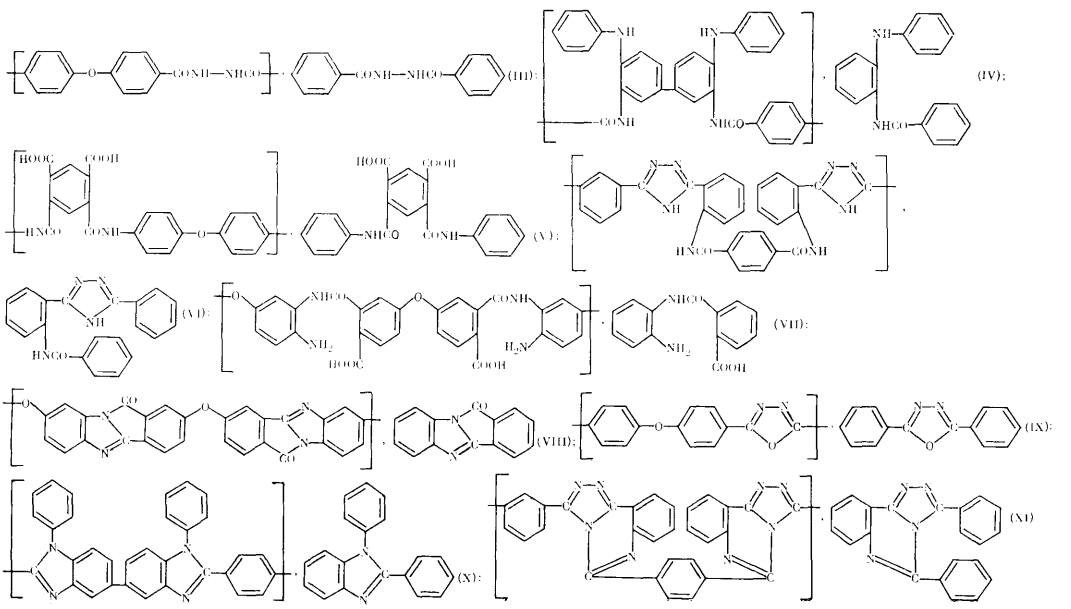
It has already been stated that this approach yields a probable correlation error less than 1% for vinyl polymers. In an approach of this kind the calculation of the enthalpy of formation of an individual polyheteroarylene can be achieved knowing only the difference between the heats of formation $\Delta(\Delta H^0_{form})$ for a reference polymer–model pair and the heat of formation of the model corresponding to the polyheteroarylene. The authors[19] chose as the reference pairs various derivatives of poly-*p*-phenylene and the corresponding aromatic compounds, while the models chosen for polyheteroarylenes were compounds already investigated thermochemically[82–88] and the data for poly-*p*-phenylene were obtained[19] by extrapolating the properties in the polymer-analogue series of compounds with $n = 1, 2, 3$.

The results of such calculations are presented in Table 7, where the following designations for the polymer–model (P_i, M_i) correlation pairs were used:

Table 7. The enthalpies of formation of polyheteroarylenes (kJ mol^{-1}).

Correlation pair (P_i, M_i)	Phase	ΔH^0_{form} (298, M)	ΔH^0_{form} (298, P)	ΔH^0_{form} (298, P)	Method
		modelling (Ref.19)		experiment	
(III)	L	—	—		—
	Am-Cr	—	—	−307.9 [82]	R
	Cr	−201.7 [82]	−312.1	—	—
(IV)	L	39.7 [84]	52.3	—	—
	Am-Cr	—	—	65.7 [85] 110.9 [84]	R
	Cr	−9.6 [83]	−36.8	—	—
(V)	L	—	—	—	—
	Am-Cr	—	—	−1039.3 [85]	R
	Cr	−907.9 [85]	−1018.4	—	—
(VI)	L	—	—	—	—
	Am-Cr	—	—	199.6 [86]	R
	Cr	94.6 [86]	110.5	—	—
(VII)	L	—	—	—	—
	Am-Cr	—	—	−935.5 [87, 88]	CC
	Cr	−481.2 [87]	−1184.9	—	—
(VIII)	L	—	—	—	—
	Am-Cr	—	—	270.3 [87, 88]	CC + D
	Cr	66.9 [87]	−87.0	—	—
(IX)	L	—	—	—	—
	Am-Cr	—	—	6.7 [82]	R + D
	Cr	75.7 [82]	−34.7	—	—
(X)	L	324.7 [84]	621.7	—	—
	Am-Cr	—	—	641.0 [83]; 709.2 [84]	R + D
	Cr	296.6 [84]	575.3	—	—
(XI)	L	433.5 [84]	769.0	—	—
	Am-Cr	—	—	795.4 [86]	R + D
	Cr	399.2 [84]	719.6	—	—

Notation. CC is combustion calorimetry, CC + D is the combustion method combined with the study of the dehydration pressure, R is reaction calorimetry, R + D is the method of reaction calorimetry combined with the study of the dehydration pressure.
Note. L = liquid, Am-Cr = amorphous-crystalline, Cr = crystalline. The numbers in square brackets denote references (Ed.of Translation).



The authors[19] suggest that, by comparing the heats of combustion and formation of polyheteroarylenes calculated in this way by the modelling method and found experimentally, it is possible not only to eliminate certain erroneous experimental data but also to estimate the degree of defectiveness of the chemical structures of the polymer studied. However, one should note that both these problems have a solution only when fairly reliable thermochemical data are available for the individual compounds modelling the repeating fragments in the structures of the polyheteroarylenes, because the accuracy of the calculated characteristics of polymers is determined primarily by the accuracy of the experimental data for the models themselves.

Table 7 compares the experimental[82–88] and calculated[19] enthalpies of formation of nine polyheteroarylenes. The results of the calculations refer to two limiting phase states of the polymers—liquid (three polymers) and crystalline (nine polymers) and the experimental values refer in all cases to an undefined amorphous-crystalline state which in the case of polymers of this kind usually corresponds to an amorphous structure of the specimen and is designated by the authors[82–88] as the solid or condensed phase. For three of the nine polyheteroarylenes indicated in Table 7 (Entries No.2, 8, and 9), the discrepancies between the experimental[83,85,86] and calculated[19] heats of formation for the corresponding liquid-amorphous states lie within a narrow range (13–26 kJ mol^{-1}), which differs little from the range of experimental errors in the heats of formation of these polymers.

However, two additional experimental results,[84] presented in Table 7 for poly[*N*-terephthaloylbis(*N'*-*o*-phenylenediamine)] (No.2) and poly[2,2'-(*p*-phenylene)-1,1'-diphenyl-5,5'-dibenzimidazole] (No.8) can hardly be regarded as correct, as can be seen from their comparison with other experimental data[83] and calculated results. In all the remaining cases the data obtained by the modelling method refer solely to the crystalline polymer and the experimental quantities refer to an undefined amorphous-crystalline state. For this reason, certain difficulties arise in their comparison. Naturally, the difficulties can be partly obviated by estimating with the aid of Bondi's empirical rule ($\Delta H^0_{fu}/T_{fu} = 12.55 + 0.46V_m$, where V_m is the molecular volume) the heats of fusion of the models and then carrying out a rough estimate by Eqn.(30) of the corresponding heats of fusion of the polymers. According to this estimate, the changes in the heats of fusion of the group of nine polyheteroarylenes considered are in the range 40–80 kJ mol^{-1}. Since the observed discrepancies between the experimental and calculated heats of formation of four of the nine polymers (Nos.1, 3, 4, and 7, Table 7) fall within the above range, the discrepancies can probably be accounted for by the influence of the difference between the phase states of the polymers compared and in the case of polyhydrazide (No.1) and poly(*p*,*p'*-diphenyl oxide)pyromellitic acid amide (No.3) relatively small discrepancies in the given characteristics may actually indicate a certain amount of order in the real polymer structures.

Since in the case of the poly-*o*-aminoamidoacid (No.5) and pyrrone (No.6) discrepancies between the experimental and calculated enthalpies of formation exceed severalfold (by a factor of 3–4) the upper limit of the above range of heats of fusion, the authors[19] actually attributed them to the influence of the chemical defectiveness, which had not been taken into account, on the properties of real polymer structures. They actually used this factor to estimate the degree of defectiveness of the chemical structure of the poly-*o*-aminoamidoacid. Korshak and co-workers[19] made an approximate estimate of the content of defective structural elements in the real specimen of the poly-*o*-aminoamidoacid from its heat of combustion[87,88] and the heats of combustion (formation) calculated by the modelling method for pure poly-*o*-aminoamidoacid and poly-*o*-aminoimide (the main types of chemical defects in the initial polymer). It was found that the content of the main homopolymer units in the specimen was only 70 wt.% and that of the "extraneous" poly-*o*-aminoimide units was 30 wt.%.

Comparison of the different experimental procedures for the determination of the enthalpies of formation of polyheteroarylenes with the aid of the data in Table 7 shows that the most reliable method for the determination of this characteristic of polymers, synthesised by a single-state polycondensation process, involves calorimetric study of the synthetic reactions of the given systems. Combustion calorimetry yields in this instance less reliable results. For those polyheteroarylenes which are the products of the thermal cyclodehydration of the initial polycondensation polymers (two-stage synthesis), the best results are obtained via a two-stage method for thermodynamic studies involving the application of combustion calorimetry in the first stage. For this reason, in order to estimate the heat of formation of the initial polyfunctional polymer, in a number of studies[82,83,86] the authors were forced to investigate calorimetrically the synthesis of the polymer and also the thermodynamic characteristics of the corresponding reactants. The temperature dependence of the cyclodehydration pressure of the initial polymer was determined in the second stage, which made it possible to find the enthalpy of the cyclodehydration process. The enthalpy of formation of the final product was then determined with the aid of Hess's cycle taking into account the enthalpies of the intermediate processes.

Thus the data considered above show that, together with the traditional classical phenomenological methods for the calculation of the thermodynamic properties of polymers, it is nowadays possible to employ successfully methods involving their modelling on the basis of data obtained for low-molecular-weight analogues. Different versions of these methods (the method of linear correlations of properties, the method of the difference interpolation of the properties of substituted polymers, and certain versions of the method of extrapolation of properties in polymer-analogue series of compounds) are sufficiently exact and universal.

On the basis of the methods indicated, it is possible to predict successfully the thermodynamic parameters not only of polymers with a simple chemical structure but also of relatively complex polyconjugated structures, namely aromatic polymers and polyheteroarylenes, to which is has so far been impossible to apply any other known approaches. The modelling methods can also be used to calculate the bond strengths in polymer macromolecules and to predict their thermal stability.

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