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Advances in the Thermodynamics of Organic Compounds in the USSR

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The results of the determination of the thermochemical parameters of organic and organometallic compounds as well as studies on the thermodynamic criteria of the occurrence of polymerisation and polycondensation processes and reactions involving products of petrochemical synthesis, carried out in the USSR during 1971-1975, are described.
The bibliography includes 114 references.

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I. INTRODUCTION

In order to lay the scientific foundations of the technology for the synthesis of new substances with the aim of obtaining materials having specified properties, it is necessary to determine optimum conditions, in the thermodynamic sense, for the new processes, i.e. conditions ensuring the optimum yield of products. It is therefore necessary to determine the enthalpies of formation and the entropies of many new substances and to calculate the Gibbs free energies of new processes as a function of temperature, pressure, and the reactant concentrations. Experimentally, this is mainly associated with the development of calorimetric research into the enthalpies of reaction and the temperature dependence of the heat capacities of substances. It is also extremely important to investigate phase equilibria involving new pure compounds and multicomponent systems of technological importance.

Since it is impossible to reflect the specific advances in all the fields indicated above in a single review, mainly studies on several fundamental subjects will be considered: studies on the enthalpies of combustion and formation of organic and organometallic compounds; measurements of their low-temperature heat capacities and thermodynamic functions; studies on the thermodynamics of a number of processes.

These investigations were carried out in the laboratories of thermodynamics and thermochemistry of Moscow, Gorky, and Belorussian State Universities, the Institute of Chemical Physics of the USSR Academy of Sciences, the State Institute of Applied Chemistry, the Mendeleev Moscow Institute of Chemical Engineering, the Kuibyshev Polytechnic Institute, and a number of laboratories of higher educational establishments and academic and industrial research institutes.

During the period indicated above, our laboratories have successfully applied new precision USSR produced apparatus—a bomb calorimeter rotating simultaneously about two mutually perpendicular axes, constructed by Kolesov[1], and a calorimeter with a microfurnace within the bomb, constructed by Gal'chenko[2] (Moscow State University); apparatus for the measurement of heat capacities from 4 K based on a special cryostat at the Physicotechnical Low-Temperature Institute of the Academy of Sciences of Ukrainian SSR[3] and a universal thermophysical apparatus of the VNIIFTRI (All-Union Institute of Physicotechnical and Radiotechnical Measurements)[4]; a differential automatic calorimeter (DAK-1) for the determination of the enthalpies of mixing of the SKB [synthetic rubber bureau (?)] of the USSR Academy of Sciences[5], and other apparatus. In particular automation designed to maintain precise adiabatic conditions in the measurements of the heat capacities in the above apparatus and the treatment of the results on a computer made it possible to increase significantly the productivity of the experiments.

There have been significant methodological advances. These involve the improvement of the technique of the combustion of gaseous and condensed of organic and fluoro- and chlorofluoro-compounds (Kolesov, Moscow State University[6]), the development of methods for the determination of the enthalpies of combustion of carbaboranes based on an explosive process (Gal'chenko, Moscow State University[7]), and the development of a novel technique for the determination of enthalpies of sublimation in a Calvet microcalorimeter[8] in relation to organoboron compounds (Moscow State University and the Institute of Chemical Physics of the USSR Academy of Sciences), and others.

In most of the studies adequate attention has been devoted to the purification and monitoring of the purity of substances and the estimation of errors of measurements. The purity in the relevant instances was not less than 99.9%; the error in the measurement of the enthalpies of combustion was 0.01-0.05%, depending on the nature of the substances, and that in the heat capacities was 0.2 to 0.5%, depending on the temperature range.

II. ENTHALPIES OF COMBUSTION AND FORMATION†

Mainly traditional studies on organohalogen and organoboron compounds have been continued at the Luginin Thermochemical Laboratory (Moscow State University). Table 1 presents the results of the determination of the enthalpies of combustion (ΔH°_c) and formation (ΔH°_f) of 19 organic chlorofluoro-compounds studied by Kolesov

† Throughout the text below, 1 cal = 4.1840 J, (g) or g denotes a gas, (liq) or liq denotes a liquid, (c) or c denotes a crystal, soln denotes a solution, v-e denotes the viscoelastic state, and v denotes the vitreous state. The superscript 0 to the thermodynamic functions indicates a standard state of 101.325 kPa.

and coworkers[6,9-14] (chlorofluoroalkanes and oxygen-containing organofluorine compounds — derivatives of alcohols, acids, ethers, and esters). The experimental data were used to determine the enthalpies of formation of fluoroethylenes, to select reference quantities for the calculation of the $\Delta H°_f$ of fluoro- and chlorofluoroalkanes by the method of group contributions, and to establish for oxygen compounds in what cases and to what extent the mutual influence of the electrophilic atoms and groups is manifested in the energy of formation of molecules. In 1976 Kolesov wrote a critical review on the thermochemistry of halogenomethanes[14]. Using his own and literature experimental data, he selected 17 reference values of $\Delta H°_f$ and calculated by the method of group contributions the enthalpies of formation of all the 70 halogenomethanes. Many of the halogenoalkanes are used in industry and their enthalpies of formation are necessary for technological calculations.

Table 1. The enthalpies of combustion and formation of organic chlorofluoro-compounds at 298.15 K.

Compound	$-\Delta H°_c$*, kcal mole^{-1}	$-\Delta H°_f$ (liq; c), kcal mole^{-1}	$-\Delta H°_f$ (g), kcal mole^{-1}	Refs.
$CH_2 = CHF$(g)	300.20±0.4	—	32.5	9
CF_3CHFCl(g)	298.22±0.6	—	74.1	11
$CF_3CH_2CH_2Cl$ (liq)	359.52±0.22	191.04±0.22	184.03	9
$CF_3CH_2CHCl_2$ (liq)	324.34±0.27	197.89±0.27	189.75	6
$CF_3CH_2CCl_3$ (liq)	295.01±0.22	198.53±0.22	189.83	9
$CF_3CH_2CF_3$ (g)	271.0±1.7	—	331.5	9
$CF_3CH_2CF_2Cl$ (liq)	288.27±0.17	278.36±0.18	271.94	11
CF_3CH_2OH (liq)	196.06±0.19	220.55±0.19	210.21	9
$CF_3CF_2CH_2OH$ (liq)	274.79±0.68	319.90±0.68	308.99	9
$CF_3(CF_2)_2CH_2OH$ (liq)	323.46±0.16	263.27±0.16	253.13	9
$CF_3CH_2CH_2OH$ (liq)	349.57±0.38	229.41±0.39	217.81	9
$CHF_2CF_2CH_2OH$ (liq)	323.46±0.16	263.27±0.16	251.28	9
$(CF_2)_4(CH_2OH)_2$ (c)	592.0±1.1	513.3	492.0	12
CF_3COOH (liq)	94.9±0.4	253,4±0.4	244.2	6,13
$CF_3CF_2COOCH_3$ (liq)	342.88±0.41	345.84±0.42	337.54	10
$(CF_2)_5C(COOCH_3)_2$ (liq)	647.0±1.0	468.4	459.1	10
$(CF_3CH_2CH_2)_2O$ (liq)	700.97±0.24	388.65±0.25	378.85	10
$(C_4F_9)_2O$ (liq)	561.78±0.73	946.8±0.7	937.1	13
$(C_5F_{11})_2O$ (liq)	721.5±3.6	1143.2	1131.9	13

* The final state for $\Delta H°_c$ was as follows: CO_2(g), H_2O.(liq), HCl(soln), HF(soln), and N_2(g).

Table 2 lists the enthalpies of combustion and formation of a number of representatives of 15 organoboron compounds of different classes studied by Gal'chenko and coworkers[2,7,8,15-17] [the carbaboranes $B_{10}C_2H_{12}$ and their derivatives, whose molecules contain a closed skeleton (nucleus) of boron and carbon atoms; acyclic aminoboranes; dialkyl-(γ-aminopropyl)boranes — boron–nitrogen inner complexes in which ring closure takes place via the N–B bond; azaborolidines and oxaborolanes— compounds with a five-membered ring incorporating B and N or B and O atoms respectively]. Apart from their independent importance, the results of these studies, continuing the many years of research by Gal'chenko into the thermochemistry of boron compounds, made it possible to discover and explain many regularities in the properties of these substances. In particular, it is of interest that the enthalpies of isomerisation of unsubstituted carbaboranes proved to be comparatively large. For the ortho → meta and meta → para transitions involving gaseous carbaboranes, they are almost identical and amount to ~ -17 kcal mole^{-1}. According to the authors, this suggests that the *para*-isomer is much more stable than the meta-isomer and the latter is more stable than the *ortho*-isomer. The enthalpies of cyclisation of dialkyl-(γ-aminopropyl)-boranes also proved to be large. The enthalpy in the liquid state is -18 kcal mole^{-1}, which accounts for the existence of cyclic compounds, while the corresponding acyclic compounds cannot be isolated. The strain in a five-membered ring with two heteroatoms, namely B and N and B and O, has been estimated as 6 ± 2 kcal mole^{-1}, which agrees with the strain energy in cyclopentane (according to the authors, due to the similarity of the atomic radii of C, O, N, and B).

Table 2. The enthalpies of combustion and formation of organoboron compounds at 298.15 K.[15,17]

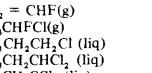
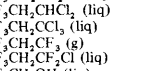
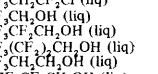
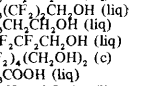
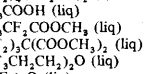
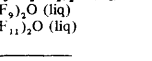
Compound	$-\Delta H°_c$, kcal mole^{-1}	$-\Delta H°_f$, kcal mole^{-1}
o-$B_{10}C_2H_{12}$ (c)	2148.0±1.6	42.4±3.5
m-$B_{10}C_2H_{12}$ (c)	2131.1±1.5	59.3±3.4
p-$B_{10}C_2H_{12}$ (c)	2114.4±1.8	76.0±3.6
1-CH_3-o-$B_{10}C_2H_{11}$ (c)	2291.1±1.3	60.8±3.9
1,2-$(CH_3)_2$-o-$B_{10}C_2H_{10}$ (c)	2446.7±1.9	68.4±3.6
1-(CH_2OH)-o-$B_{10}C_2H_{11}$ (c)	2270.0±1.7	82.7±3.5
1-(COOH)-o-$B_{10}C_2H_{11}$ (c)	2153.3±2.0	131.1±3.7
$(n\text{-}C_3H_7)_2BN(n\text{-}C_3H_7)_2$ (liq)	2140.2±1.4	104.1±1.4
$(n\text{-}C_4H_9)_2BN(n\text{-}C_4H_9)_2$ (liq)	2766.8±1.6	126.9±1.6
	1617.7±2.2	71.1±2.2
	1615.8±1.7	73.1±1.7
	1682.1±2.0	75.1±2.0
	1988.4±2.0	93.5±2.1
	2003.8±1.6	78.1±1.6
	1222.4±0.7	107.6±0.7

Table 3. The enthalpies of formation of tricyclopentadienyl-lanthanide complexes[19] at 298.15 K.

Compound	$\Delta H°_f$, kcal mole^{-1}	Compound	$\Delta H°_f$, kcal mole^{-1}
$Sc(C_5H_5)_3$ (c)	−3,2±1	$Pr(C_5H_5)_3$ (c)	−6.7±2
$Y(C_5H_5)_3$ (c)	−10.8±1	$Tm(C_5H_5)_3$(c)	−11.8±1
$La(C_5H_5)_3$(c)	−6.4±1	$Yb(C_5H_5)_3$ (c)	7.0±1

The enthalpies of combustion and formation of 38 organic compounds of transition metals [tricyclopentadienyl-lanthanides (Table 3); dicyclopentadienyl compounds of metals of the 3*d* series; dicyclopentadienyl complexes of molybdenum, tungsten, zirconium, and hafnium hydrides, chlorides, and iodides (Table 4); alkylcyclopentadienyl and cyclopentadienyl phenyl compounds of titanium, zirconium, and platinum; arene derivatives of chromium; niobium and tantalum alkoxides (Table 5)] were determined by Rabinovich, Tel'noy, and coworkers at the Termochemical Laboratory of Gorky

State University[18–25]. The purity of these compounds was 99.97–99.99%. Special measures were taken to prevent their oxidation before combustion. The solid combustion products were determined chemically and by X-ray diffraction. The error of the determination of the enthalpy of combustion was 0.02–0.05%.

Table 4. The enthalpies of formation of dicyclopentadienyl complexes of metals of the 3*d* series[20,23] at 298.15 K.

Compound	ΔH_f^0, kcal mole^{-1}
$(C_5H_5)_2Cr$ (c)	42.7±0.5
$(C_5H_5)_2Mn$ (c)	48.0±0.5
$(C_5H_5)_2Fe$ (c)	40.2±0.4
$(C_5H_5)_2Co$ (c)	56.5±0.5
$(C_5H_5)_2Ni$ (c)	68.2±0.4
$(C_5H_5)_2MoH_2$ (c)	46.6±0.6
$(C_5H_5)_2WH_2$ (c)	59.9±0.6
$(C_5H_5)_2ZrCl_2$ (c)	−128.1±0.6
$(C_5H_5)_2HfCl_2$ (c)	−128.6±0.7
$(C_5H_5)_2MoCl_2$ (c)	−22.9±0.6
$(C_5H_5)_2WCl_2$ (c)	−17.0±0.6
$(C_5H_5)_2MoI_2$ (c)	7.2±0.5
$(C_5H_5)_2WI_2$ (c)	28.0±0.7

Table 5. The enthalpies of formation of a number of transition metal compounds[21,23,25] at 298.15 K.

Compound	ΔH_f^0, kcal mole^{-1}
$(C_5H_5)_2Ti(CH_2C_6H_5)_2$ (c)	46.8±1.2
$(C_5H_5)_2Zr(CH_3)_2$ (c)	−10.6±0.5
$(C_5H_5)_2Zr(C_6H_5)_2$ (c)	65.9±2.6
$(C_5H_5)Pt(CH_3)_3$ (c)	40.3±0.5
$(C_5H_5)_2Pt(CH_3)_2$ (c)	31.2±1.7
$(C_6H_5C_2H_3)_2Cr$ (liq)	15.9±1.0
$[C_6H_4(C_2H_5)_2]_2Cr$ (liq)	−11.3±1.9
$[C_6H_4(C_2H_7)_2]_2Cr$ (liq)	−46.7±2.0
$(CH_3O)_5Nb$ (liq)	337.9±0.6
$(C_2H_5O)_5Nb$ (liq)	378.6±0.6
$(C_3H_7O)_5Nb$ (liq)	406.7±0.9
$(CH_3O)_5Ta$ (liq)	338.8±0.6
$(C_2H_5O)_5Ta$ (liq)	391.6±0.7
$(C_3H_7O)_5Ta$ (liq)	420.5±1.0

The enthalpies of formation of the above substances in the condensed state and the data in Refs. 18–25 or those of other workers for the enthalpies of sublimation or vaporisation were used to calculate the enthalpies of formation in the gaseous state and from the latter the average dissociation energies of many bonds formed by transition metals in their organic derivatives were calculated. Together with the results of calculations from thermochemical data in the literature for metal carbonyls and several alkoxides, these results are presented in Figs. 1–3.[23] In all cases the average dissociation energy of the M–L bond in the compounds ML_n with the same ligand and identical values of n increases down the Groups of the Periodic System as the atomic number of the metal increases. This is particularly interesting in view of the fact that the opposite variation has been observed for organic derivatives of non-transition elements (E) — the average dissociation energy of E–R bonds decreases in the compounds ER_n with the same R and n down the Groups of the Periodic System as the atomic number of the element increases (Fig. 4).[26] Clearly this behaviour of transition metal compounds is due to the specific features of the variation of their effective nuclear charge and of the configuration of the electron shell in the subgroups of the Periodic System. We established that similar opposed variations are observed also for inorganic compounds of transition and non-transition elements[26].

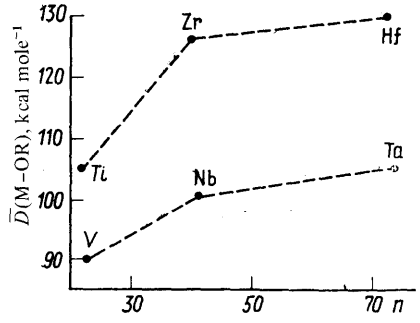


Figure 1. Dependence of the dissociation energy of M–OR bonds in transition metal alkoxides on the atomic number of the metal n.[26]

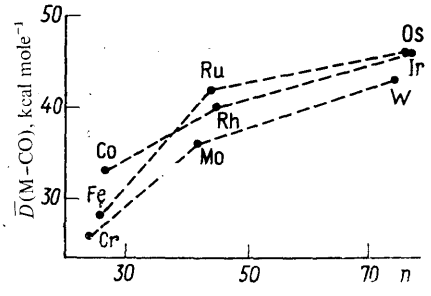


Figure 2. Dependence of the average dissociation energy of the M–CO bonds in metal carbonyls on the atomic number of the metals n.[26]

The enthalpies of combustion and formation of a further 54 organic compounds of metals, including 24 different silicon compounds, some of which are listed in Table 6, 14 germanium compounds (Table 7), and certain tin, aluminium, mercury, and magnesium compounds have been measured in the USSR. Most of these studies were carried out in Kostryukov's[27–30], Gadzhiev's[31–33], Shaulov's[34–42],

and the author's[43–47] laboratories. Tel'noy and Rabinovich wrote a review of the Soviet and foreign studies on the thermochemistry of organic compounds of transition metals[23].

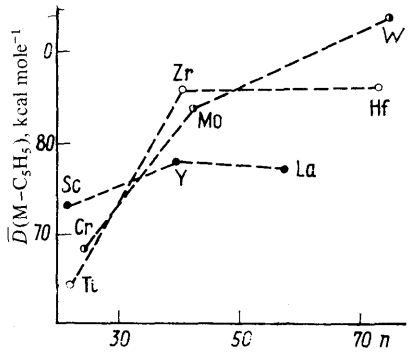


Figure 3. Dependence of the average dissociation energy of the M–C_5H_5 bonds in dicyclopentadienyl derivatives of transition metals on the atomic number of the metal n.[26]

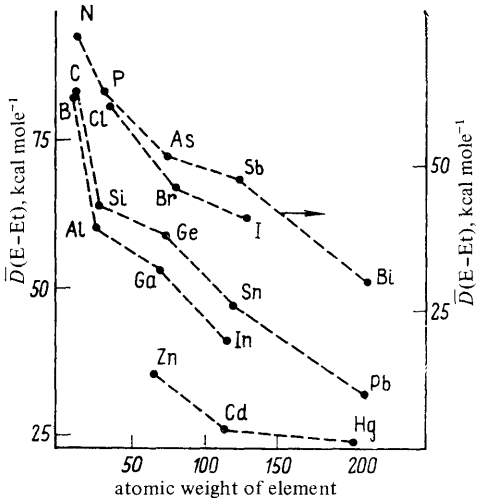


Figure 4. Dependence of the average dissociation energy of the element (E)–ethyl group (Et) bonds in the compounds EEt_n of non-transition elements on the atomic number of the element n.[26]

The enthalpies of combustion and formation of ~100 organic nitrogen compounds of different classes have been determined in Lebedev's[48–52] and Lebedeva's[53–57] laboratories. These are nitrohydrocarbons, alkylamines, amides, and nitriles, nitro- and amino-acids, as well as other compounds which are of considerable theoretical and applied interest. Finally, in this section we may mention studies on non-aromatic bicyclic and polycyclic compounds, which are being carried out systematically by Kozina and Gal'chenko at Moscow State University[58–60]. Together with their coworkers, they determined the enthalpies of combustion and formation of ~15 substances belonging mainly to the bicyclo[2,2,1]heptane (norbornane) and bicyclo[4,1,0]heptane (norcarane) series (Table 8). The energetics of these compounds are of considerable theoretical interest and some of them are used in industry.

Table 6. The enthalpies of formation of a number of organosilicon compounds at 298.15 K.

Compound	ΔH_f^0, kcal mole^{-1}	Refs.
$(C_2H_5)_3SiN(C_2H_5)_2$ (liq)	−88±1	43
$(CH_3)_2(C_2H_5O)Si(CH_2)_3NH_2$ (liq)	−154±2	35
$[(C_2H_5)_2N]_3SiH$ (liq)	−131±1	43
$(CH_3)_3SiOOC(CH_3)_3$ (c)	−126±3	44
$(C_2H_5)_6Si_2Hg$ (liq)	−40±1	45
CH_3SiCl_3 (liq)	−145.5±1.1	31
$(CH_3)_2SiCl_2$ (liq)	−116.8±0.8	31
$(CH_3)HSiCl_2$ (liq)	−104.0±1.0	31
$(C_2H_5)_4Si$ (liq)	56.8±1.7	31
$(C_6H_5)_2SiCl_2$ (liq)	−48.2±2.7	
$(C_6H_5)_3SiCl$ (c)	12.5±4.1	31

Table 7. The enthalpies of formation of a number of organogermanium compounds at 298.15 K.

Compound	ΔH_f^0, kcal mole^{-1}	Refs.
$(CH_3O)_4Ge$ (liq)	205.5±0.4	39
$(C_2H_5O)_4Ge$ (liq)	244.8±0.5	39
$(C_6H_5O)_4Ge$ (liq)	112.7±1.0	39
$(C_2H_5)_6Ge_2O$ (liq)	148±4	44
$(C_2H_5)_3GeOOC(CH_3)$ (liq)	120.4±1.3	44
$(n\text{-}C_4H_9)_4Ge$ (liq)	91.7±1.2	37
$(C_2H_5)_3GeN(C_2H_5)_2$ (liq)	86±1	43
$[(CH_3)_2GeO]_4$ (c)	378.7±1.5	27
$[(C_2H_5)_2GeO]_4$ (c)	379.8±5.2	29
$(C_2H_5)_6Ge_2Hg$ (liq)	32±1	45
$(C_3H_7)_6Ge_2Hg$ (liq)	74±1	45

In all, the enthalpies of formation of ~95 organic derivatives of metals were determined in the Soviet Union during 1971–1975, while in other countries similar determinations were made for altogether ~120 compounds.

III. THE LOW-TEMPERATURE HEAT CAPACITY AND THERMODYNAMIC FUNCTIONS

The temperature dependence of the heat capacities of 12 organoelemental compounds, including seven cyclopentadienyl derivatives of transition metals of the 3*d* series, in the range 5–300 K,[60–62], and 17 alkyl, carbonyl, and bisarene derivatives of metals in the range 60 to 300 K[60–62] were determined by Nistratov, Shaiman, and Maslova at the Thermochemical Laboratory of Gorky University. The thermodynamic functions of the above substances were calculated and the parameters of fusion

and transitions in the solid state were determined. Table 9 lists the entropies of the organoelemental compounds calculated from the temperature variation of the heat capacity.

Table 8. The enthalpies of formation of hydrocarbons of the norbornane and norcarane series[57–59] at 298.15 K.

Hydrocarbon	ΔH_f^0, kcal mole^{-1}	Hydrocarbon	ΔH_f^0, kcal mole^{-1}
cis, cis-Cycloocta-1,5-diene (liq)	13.78±0.33	7,7-Dimethylnorbornane (s)	−35.43±0.39
cis-Carane (liq)	−27.72±0.55	Nortricyclene (s)	7.42±0.27
trans-Carane (liq)	−28.33±0.61	Norbornene (s)	9.89±0.34
3-Carene (liq)	−7.06±0.45	7-Methylenenorbornane (liq)	4.7±0.5
2-Carene (liq)	−5.41±0.57	Camphene (s)	−18.01±0.53

Table 9. Thermodynamic functions of organoelemental compounds at 298.15 K[60–62] (calculations based on the heat capacities measured in the range 5–300 K)

Compound	$H^\circ(298.15) - H^\circ(0)$, kcal mole^{-1}	S°, kcal mole^{-1}	Compound	$H^\circ(298.15) - H^\circ(0)$, cal mole^{-1} K^{-1}	S°, cal mole^{-1} K^{-1}
$Hg(C_5H_5)_2$	10.28	67.44	$Mn(C_5H_5)_2$	8.34	60.08
$In(C_5H_5)_3$	14.55	88.67	$Co(C_5H_5)_2$	7.81	56.42
$Si(C_5H_5)_4$	15.52	98.44	$Ni(C_5H_5)_2$	8.25	60.47
$As(C_5H_5)_3$	12.90	84.48	$(C_5H_5)_2Ti(OCOC_6H_5)_2$	18.59	129.9
$V(C_5H_5)_2$	7.92	57.40	$(C_5H_5)_2HfCl_2$	10.27	73.27
$Cr(C_5H_5)_2$	7.71	56.40	$(C_5H_5)_2CrI$	10.18	74.54

Fairly distinct λ-transitions in the solid state were observed in the dicyclopentadienyl derivatives of vanadium, chromium, cobalt, and nickel; like the transitions known previously for ferrocene[63], these are transitions of the order–disorder type and are due to the manifestation of the hindered rotation of the ligands ‡. (Fig. 5 illustrates the λ-transitions in chromocene and cobaltocene).

‡ The rotation of the cyclopentadienyl rings, which alters their mutual intramolecular orientation, causes a significant change in the energy of the interaction of the rings of neighbouring molecules in the crystal lattice.

It is striking that the above compounds can be arranged in a series in terms of the enthalpies of the transitions (Table 10), which differs little from the series based on the absolute negative charges on the metal atoms, calculated by Armstrong et al.[64] The ratios of the hindered and eclipsed conformations of the molecules in each of the above four compounds were determined from the enthalpies of the transitions (Table 10). Here $\Delta S_t = R \ln X < R \ln 2$, where $X = 1.39$, 1.36, 1.17, and 1.16 for the cobalt, chromium, nickel, and vanadium compounds respectively ($X = 1.89$ for ferrocene).

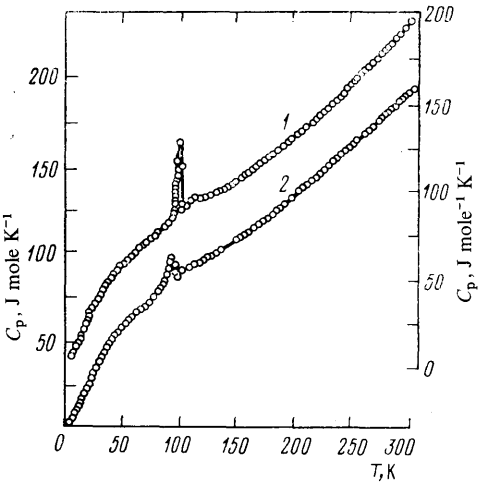


Figure 5. Occurrence of the λ-transitions in solid chromocene (curve *1*) and cobaltocene (curve *2*) on the curves representing the temperature variation of their heat capacities[65].

Table 10. Parameters of the λ-transitions of dicyclopentadienyl derivatives of transition metals of the 3*d* series[62].

Compound	T, K	ΔH_t^0, cal mole^{-1}	ΔS_t^0, cal mole^{-1} K^{-1}
$Fe(C_5H_5)_2$*	125—200	204	1.27
$Cr(C_5H_5)_2$	75—140	63.3±0.8	0.61±0.01
$Co(C_5H_5)_2$	70—120	56.8±0.5	0.65±0.01
$V(C_5H_5)_2$	120—200	46.8±0.5	0.29±0.01
$Ni(C_5H_5)_2$	100—190	43.4±0.5	0.32±0.01

* Data of Edwards et al.[63] (quoted for comparison with the parameters of the λ-transitions of other 3*d* metals).

It is of interest that the entropy of the λ-transition in dicyclopentadienyltitanium dibenzoate[65] proved to be $\sim R \ln 4$ ($\Delta S_t = 2.75$ cal mole^{-1} K^{-1}), which corresponds to the presence of four molecular conformations above the transition temperature, while there is only one conformation below this temperature. Presumably, two of the four conformations arise owing to the hindered rotation of the cyclopentadienyl rings and two are due to the rotation of the benzoate groups ($\Delta H_t = 392.5$ cal mole^{-1}).

The Gibbs free energies of the direct synthesis of the dicyclopentadienyl derivatives of metals of the 3*d* series as well as their thermal decomposition reactions, which are of interest for the preparation of the pure metals, were calculated from the enthalpies and entropies of formation of the compounds. Fig. 6 shows that the points of intersection of curves *1–6* with curves *7* and *8* determine the lower limits of the temperature ranges in which the above reactions are allowed for different metals at the standard pressure. It is therefore of interest that the coworkers of Academician G. A. Razuvaev (Institute of Chemistry of the USSR Academy of Sciences, Gorky) carried out direct syntheses of a number of cyclopentadienyl and arene derivatives from gaseous metals and solid hydrocarbons *in vacuo* at the temperature of liquid nitrogen[66] on the basis of analogous calculations using the data in Refs. 61–63.

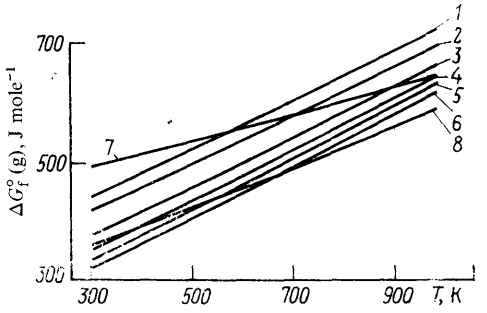


Figure 6. Graphical determination of the temperature ranges in which the reactions $M(g) + 2C_5H_6(g) \rightarrow (C_5H_5)_2.M(g) + H_2(g)$ and $(C_5H_5)_2M(g) \rightarrow M(g) + 2C_5H_5(g)$ at a pressure of 101.325 kPa are thermodynamically allowed (according to the Gibbs free energies of formation of the reactants)[65]: *1)–6)* $M(C_5H_5)_2$; M: *1)* Ni; *2)* Co; *3)* Mn; *4)* Cr; *5)* Fe; *6)* V; *7)* $2C_5H_5$; *8)* C_5H_6.

Kostryukov, Karasharli, and coworkers[67–69] investigated the temperature dependence of the heat capacities and calculated the thermodynamic functions in the range 12–370 K for 13 organosilicon compounds (siloxanes, silacyclanes, and silanes), some of which are listed in Table 11. Anomalies in the solid state, associated either with the deformation of the ring made up of silicon–oxygen bonds or with the hindered rotation of the methyl groups, have been found for a number of the above compounds.

Among other studies, mention should be made of investigations of the heat capacities of a number of benzene derivatives in the gaseous state [300–670 K, 10^5 (5–250) Pa] carried out by Akhundov[70] with the aid of an adiabatic flow calorimeter (error of the measurements ~0.45–0.65%), Kolesov's measurements of the low-temperature heat capacities of chlorofluoropropanes[71], and Paukov's studies on the heat capacities of substituted hexafluorobenzenes[72]. Altogether, in the period under consideration studies were made on the low-temperature heat capacities of ~70 organic compounds; among these ~50 compounds were investigated in the temperature range from 5–12 K to 300 K.

Approximately 30 studies were devoted to the calculation of the thermodynamic functions of organic compounds in the ideal gas state from molecular constants. Among them, special mention should be made of the research by Shaulov[73,74] and Pashinkin and coworkers[75] on the calculation of the thermodynamic functions of alkyl derivatives of Group III–V elements and certain carbonyls used to prepare pure metals and semiconducting compounds.

Clearly the determination of the entropies of ~100 important compounds will be useful for the corresponding technological calculations.

Table 11. Thermodynamic functions of organosilicon compounds[67–69] (calculated from the temperature variation of the heat capacities).

Compound	$H^\circ(298.15) - H^\circ(0)$, kcal mole^{-1}	$S^\circ(298.15)$ kcal mole^{-1} K^{-1}
$(CH_3)_2SiO[(CH_3)_2SiO]_2(CH_3)_2SiO$	16.71	101.4
$(CH_3)_2SiO[(CH_3)_2SiO]_2(C_6H_5)_2SiO$	24.81	181.3
$(CH_3)C_6H_5SiO[(CH_3)C_6H_5SiO]_2(CH_3)C_6H_5SiO$	23.41	158.4
cis-$(CH_3)C_6H_5SiO[(CH_3)C_6H_5SiO](CH_3)C_6H_5SiO$	20.34	136.5
trans-$(CH_3)C_6H_5SiO[(CH_3)C_6H_5SiO](CH_3)C_6H_5SiO$	19.81	131.1
$(CH_3)Si(CH_2)_2CH_3$	10.24	68.8
$(CH_3)SiCH_2Si(CH_3)_2CH_2$	10.99	70.9
p-$Cl_3SiC_6H_5$	11.29	78.6
Cl_3SiCH_2CN	8.47	58.8

IV. THERMODYNAMICS OF POLYMERISATION AND POLYCONDENSATION PROCESSES

In connection with the needs of the rapidly developing polymer industry, a comparatively large amount of research has been done into the thermodynamics of the processes involving the synthesis of polymers. The enthalpies, entropies, and Gibbs free energies of the polymerisation of 20 carbocyclic and heterocyclic substances as well as organometallic compounds have been determined. Most of these studies were carried out by Lebedev and coworkers[76–80] at the Gorky University and in the laboratory of the present author.

It was shown that the polymerisation of certain heterocyclic compounds, which could not be polymerised hitherto, is thermodynamically allowed. This applies particularly to *N*-(β-trimethylsilylethyl)ethyleneimine and the analogous derivative of trimethyleneimine, which are nowadays polymerised indirectly — via complexes with zinc chloride. Table 12 shows that the Gibbs free energies are fairly large and negative for the polymerisation of both the corresponding complexes and the individual imines. Evidently the role of complex formation reduces in these instances to decreasing the process activation energy.

Another heterocycle — 1,1,3,3-tetramethyl-1,3-disilacyclobutane — has been polymerised catalytically near the standard temperature. Cyclopentene and cyclo-octa-1,5-diene also polymerise, giving rise to new varieties of synthetic rubber, glycolide forms a polymer which is used for medical purposes, and tetrahydrofuran polymerises

Table 12. Thermodynamic parameters of the polymerisation of *N*-(β-trimethylsilylethyl)-ethyleneimine and *N*-(β-trimethylsilylethyl)trimethyleneimine directly and via complexes with zinc chloride at 298.15 K.[78]

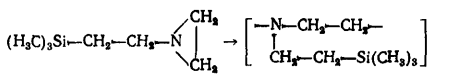
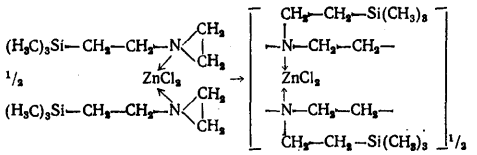
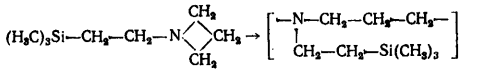
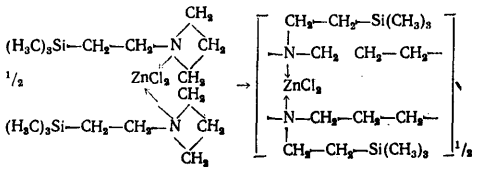
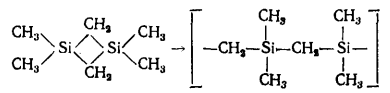
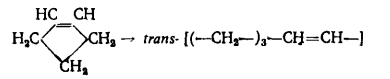
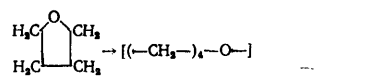
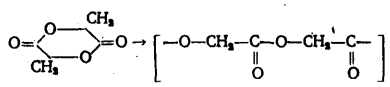
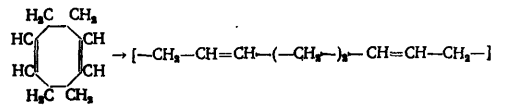
Process	State of reactants	$-\Delta H^\circ$, kcal mole^{-1}	$-\Delta S^\circ$, cal mole^{-1} K^{-1}	$-\Delta G^\circ$, kcal mole^{-1}
	liq → v-e	28.4	24.0	21.2
	c → v	31,5	3.56	30.4
	liq → v-e	27,5	19.9	21.6
	c → v	30.8	4.42	29.5

Table 13. Thermodynamic parameters of the polymerisation of certain cyclic compounds[80] at 298.15 K.

Process	*T*, K	State of reactants	$-\Delta H^\circ$, kcal mole^{-1}	$-\Delta S^\circ$, cal mole^{-1} K^{-1}	$-\Delta G^\circ$, kcal mole^{-1}
	298.15	liq → v-e	17,7	0.90	18.0
	298.15	liq → v-e	4,45	11.0	1.17
	298.15	liq → v-e	4,45	11.4	1.05
	550	liq → v-e	7,51	4.18	5.21
	298.15	liq → v-e	9.56	10.8	6.34

(Table 13). In all cases the polymerisation reaction takes place with ring opening and, in the absence of transitions involving different states of aggregation, the enthalpy of the process is close to the ring strain energy.

In the studies described the enthalpy of polymerisation was determined directly in a calorimeter or calculated from the experimental enthalpies of combustion of the polymers and monomers. The entropy of polymerisation was calculated from the temperature dependence of the heat capacities of the polymers and monomers measured from 4 or 8 K. Specimens of several of these polymers had a comparatively high degree of crystallinity: 40% for the polypentenamer, 65% for polytetrahydrofuran, and 67% for polyglycolide. The difference between the zero-point entropies of the polymers in the amorphous and crystalline states was calculated in these cases from plots of the temperature variation of the heat capacities of the fully crystalline and fully amorphous polymers obtained by extrapolating the corresponding experimental plots for the partly crystalline specimens[81]. For the polymers indicated above, the difference proved to be 3.5–4 cal mole^{-1} K^{-1}, which corresponds to approximately half the entropy of fusion of the above compounds under the conditions of 100% crystallinity. As an example, Fig. 7 presents the temperature dependence of the heat capacity of polytetrahydrofuran used to calculate the entropy.

Together with polymerisation reactions, the thermodynamics of the two-stage polycondensation synthesis of a number of polyheteroarylenes, distinguished by a comparatively high thermal stability, was investigated by Karyakin and coworkers[82–88] at the Thermochemical Laboratory of Gorky State University in collaboration with the laboratory of Academician V. V. Korshak (Institute of Organoelemental Compounds of the USSR Academy of Sciences) and the "Plastics Union". The first stage of the synthesis of these heterocyclic polymers consists in the interaction of aromatic diamines or their derivatives with acid dianhydrides in *N,N*-dimethylformamide with formation of an incompletely cyclised prepolymer. The enthalpies of these reactions were determined directly in an adiabatic calorimeter and their entropies were calculated from measurements of the heat capacities of solutions of each reactant in dimethylformamide as a function of temperature at concentrations corresponding to the polycondensation reactions. In all cases, differing in the composition of the initial amines and anhydrides, the standard Gibbs free energies of the processes at ~298 K show that their equilibria are almost completely displaced towards the formation of the prepolymers.

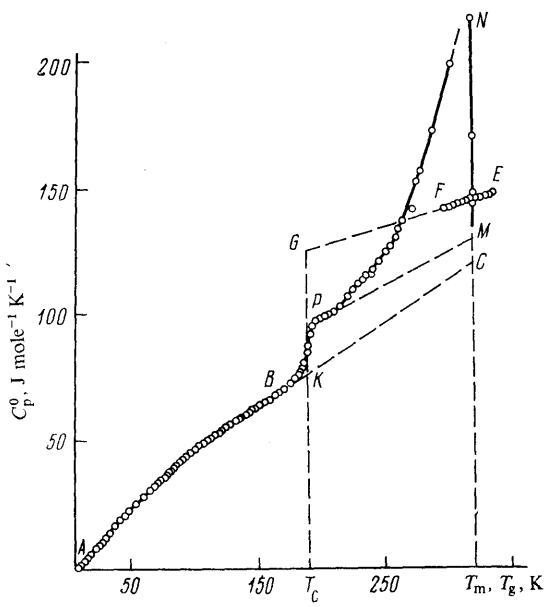
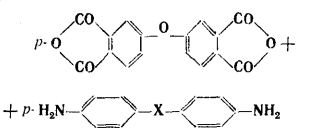


Figure 7. Temperature variation of the heat capacity of polytetrahydrofuran[80]: circles — experimental data for the polymer with a 65% degree of crystallinity; *ABKC*— experimental data for the polymer with 100% degree of crystallinity (extrapolation neglecting the difference between the heat capacities of the amorphous and crystalline polymers before devitrification); *ABPM*— experimental data for the specimen with a 65% degree of crystallinity (extrapolation); *ABGFE*— experimental data for the specimen with 0% degree of crystallinity (extrapolation); T_g and T_m are the glass and melting points respectively.

The second stage of the synthesis involves additional cyclisation of the prepolymer at elevated temperatures with evolution of water. The equilibrium constants of the cyclodehydration reaction were determined from the equilibrium vapour pressure and their temperature variation was used to find the enthalpies of the reactions. The results show that the thermodynamic criteria allow the cyclodehydration of the prepolymers to go virtually to completion over a wide temperature range. However, the reaction does not go to completion because of kinetic factors and the copolymers formed have both the final cyclic structures and the structures of the initial prepolymers. A method has been proposed for the determination of the compositions of such copolymers from their enthalpies of combustion. As an example, Tables 14 and 15 present the thermodynamic parameters of the reactions involving the formation of certain prepolymers and final polymers.

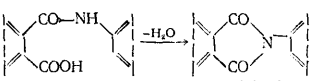
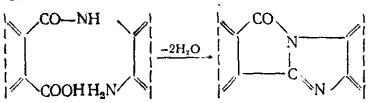
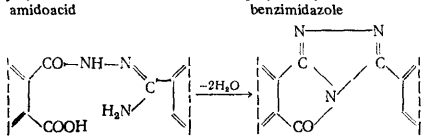
Table 14. Thermodynamic parameters of polycondensation reactions[83]:



(298.15 K; solvent — dimethylformamide)

X	$-\Delta H^0$, kcal mole^{-1}	$-\Delta S^0$, cal mole^{-1} K^{-1}	$-\Delta G^0$, kcal mole^{-1}
O	30.8	46.0	17.1
O—Ph—O	30.5	—	—
—	29.4	—	—
CO	25.3	—	—
SO_2	24.0	45.5	7.4

Table 15. The enthalpies and Gibbs free energies of the cyclodehydration of prepolymers[88] at 400 K.

Reaction	ΔH^0, kcal mole^{-1}	$-\Delta G^0$, kcal mole^{-1}
 poly(-*p,p'*-diphenyl oxide-) pyromellitimide → polyimide	15.2	7.05
 polyamino-amidoacid → polybenzoylene-benzimidazole	14.9	27.0
 poly(-O-carboxybenzyl-amidrazone) → polybenzoylene-*s*-triazole	23.5	27.9

V. THERMODYNAMICS OF REACTIONS OF PRODUCTS OF PETROCHEMICAL SYNTHESIS AND OTHER PROCESSES

In a number of higher educational establishments of the USSR studies have been made on the thermodynamics of ~150 isomerisation reactions of alkanes, alkenes, and their halogeno-derivatives (the results of some of these are listed in Table 16), the dehydrohalogenation reactions of halogeno-derivatives of alkanes and alkenes, and disproportionation reactions of alkenes. Rozhnov[89–92] (Kuibyshev Polytechnic Institute), Andreevskii and Kabo[93–96] (Belorussian State University), Vasil'eva and coworkers[97] (All-Union Petrochemical Synthesis Institute), and others studied experimentally the equilibria in the processes in the range from the standard temperature to 600 K and calculated the thermodynamic parameters of the reactions from their equilibrium constants and the temperature variation of the latter. Some of the processes investigated are already used in industry and others can be so employed. Particular mention should be made of the determinations, which are of practical importance, of the thermodynamic parameters of a number of reactions involving the pyrolysis of benzene[98], the synthesis of 4,4-dimethyl-1,3-dioxan from isobutene and formaldehyde and its conversion into isoprene[99], and the synthesis of alkylene carbonates[97] and Freon-11 and Freon-12,[100] as well as the investigation of the equilibria in the individual stages of the formation of isoprene and piperylene from isopentene[101], etc.

Table 16. The enthalpies and entropies of isomerisation of alkanes, alkenes, and their halogeno-derivatives[92–96].

Reaction	Conditions	$\overline{\Delta H^\circ}$, kcal mole^{-1}	$\overline{\Delta S^\circ}$, cal mole^{-1} K^{-1}
$CH_2Br-CH_2-CH_3 \rightleftarrows CH_3-CHBr-CH_3$	273–583 K; (liq)	−2.86±0.13	−3.66±0.38
$CH_2Br-CH(CH_3)-CH_3 \rightleftarrows CH_3-CBr(CH_3)-CH_3$	273–526 K; (liq)	−3.800±0.160	−5.8±0.5
$CH_2Cl-CH_2-CHCl-(CH_2)_2-CH_3 \rightleftarrows CH_2Cl-(CH_2)_2-CHCl-CH_2-CH_3$	273–363 K; (liq)	−0.530±0.030	0.90±0.09
erythro-$CH_3-CHCl-CHCl-CH_3 - CH_3 \rightleftarrows$ *meso*-$CH_3-CHCl-CH_2-CHCl-CH_3$	273–373 K; (liq)	1.890±0.100	2.43±0.32
$CH_2=C(CH_3)-(CH_2)_2-CH_3 \rightleftarrows CH_3-C(CH_3)=CH-CH_2-CH_3$	273–516 K; (gas) 101 kPa	−1.13±0.15	−0.30±0.35
$CH_3-CCl(CH_3)-CH_2-CH_3 \rightleftarrows CH_3-CH(CH_3)-CHCl-CH_3$	273–373 K; (liq)	1.89±0.05	1.75±0.2

Research into the thermochemistry of the complex formation reactions of organic compounds is being rigorously prosecuted in our country. Gur'yanova and Gol'dshtein and coworkers (Karpov Physicochemical Institute) investigated the formation of complexes by ethers, sulphides, selenides, amines, phenols, and organophosphorus compounds with alkyl derivatives of boron and aluminium, the halides of various elements, and other substances (for further details, see the monograph of Gur'yanova et al.[102]).

In the Thermochemical Laboratory of Gorky State University, Tsvetkov and coworkers carried out a series of studies on the thermochemistry of the interaction of alkyl derivatives of Group III–V elements with one another[103,104]. The corresponding complexes are of interest, because semiconducting compounds can be obtained from them. A large number of studies on the thermochemistry of hydrogen-bonded complexes have been described in detail in a recent review[105].

VI. LIQUID–VAPOUR EQUILIBRIA INVOLVING PURE SUBSTANCES

Data on the vapour pressures and enthalpies of vaporisation and sublimation of ~500 substances (the studies by Karapet'yants and coworkers on the precision measurements and approximate calculation of the vapour pressures of many organosilicon, organotin, and organogermanium compounds[106–108], a number of studies on the vapour pressures of linear and cyclic oligo-organosiloxanes and other organosilicon compounds with different substituents at the silicon atom[109,110], studies by Gal'chenko and Lebedev and coworkers on the direct determination of the enthalpies of sublimation of organoboron compounds[111], studies by Devyatykh and coworkers on the vapour pressures of cyclopentadienyl derivatives of the lanthanides[112], studies by Rabinovich, Kir'yanov, and coworkers on the vapour pressure of cyclopentadienyl derivatives of transition metals of the 3*d* series[20,21], studies by Baev at the Belorussian Technological Institute on the vapour pressures of alkyl derivatives of non-transition elements[113] and metal carbonyls[114], as well as those of many other investigators) were published in 1971–1975.

It is clear from the list of compounds whose vapour pressures have been investigated that they are of both theoretical and applied interest. In particular, the enthalpies of vaporisation and sublimation obtained have been used in a number of investigations to calculate the enthalpies of formation of compounds in the gaseous state from their experimental enthalpies of formation in the condensed state §.

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§ This is why we have considered briefly studies on the vapour pressures of organic compounds, while those on phase equilibria in multicomponent systems have not been examined.

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