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The interrelation between the temperature of solid decompositions and the *E* parameter of the Arrhenius equation

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Abstract

A criterion of equilibrium development for the sublimation processes has been formulated and theoretically substantiated. It is based on the ratio of sublimation temperature, T_{sub} (which corresponds to the vapor partial pressure of 10^{-7} bar), to the enthalpy of sublimation, ΔH_T°. This ratio is in the range 3.6 ± 0.2 K mol kJ^{-1} (S.D.). This criterion has been applied to the free-surface decompositions of 100 different substances including some metalloids and simple binary compounds together with metal salts of inorganic and organic acids, ammonium and hydrated salts. The experimental values of the initial temperature, T_{in}, and the E parameter, which are equivalent to the theoretical T_{sub} and ΔH_T° values, were taken from the literature. The mean value of T_{in}/E ratio for all reactants is equal to 3.6 ± 0.4 (S.D.). This means that the decomposition of all solids proceeds in agreement with the equilibrium laws. A higher deviation of T_{in}/E ratio from the mean (compared to theory) is connected with random errors in the determination of the E parameter and the uncertainty in the definition of the initial temperature of decomposition. For the first time, the third-law method was used for the purposeful calculation of the E parameters in cases of free-surface solid decompositions. The comparison of results obtained by the second- and third-law methods for 20 different reactants revealed the great advantages of the latter method in precision and accuracy of determinations and also in time spent for the experiment.

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1. Introduction

The temperature of decomposition is an important, if not the most important, kinetic parameter in investigations of solid decompositions. It determines the upper point of stability of the reactant and onset of the decomposition reaction. However, most workers in kinetic analysis use the temperature only as an auxiliary parameter in determinations of the Arrhenius parameters: A and E. So, Galwey [1] used the average temperatures of decomposition to estimate A-values on the basis of the known E parameters for different reactants. Up to now, there has been no quantitative definition of the initial temperature of decomposition based on the fixed magnitudes of decomposition rate, J, or related parameters (the rate constant, k, or the equivalent value of partial pressure of gaseous product, P). No one in thermal analysis has yet considered in detail the direct interrelationship between the decomposition temperature and the E parameter. Furthermore, Vyazovkin [2] considers the E parameter to be a variable and theoretically unpredictable function of temperature. Contrary to this pessimistic (agnostic) view, such an interrelationship has been revealed in electrothermal atomic absorption spectrometry (ET AAS).

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The proportional dependence of the initial temperature, T_{in}, of analyte atomization in graphite furnaces (which corresponds to the appearance of an atomic absorption signal) on the E parameter was pointed out on purely empirical grounds in the mid-1970s [3,4]. Recently, this has received a rigorous theoretical explanation [5–9] and application for the identification of the mechanism of analyte release in ET AAS [6,7,9] and for the validity control of measured E-values in kinetic studies [10]. This was achieved in the framework of the so-called 'physical approach' to the interpretation of the kinetics and mechanisms of thermal decomposition of solids.

The objectives of this work are, firstly, to present the experimental data from the literature which confirm the equilibrium character of solid decompositions, as occurs in the simple evaporation of liquids or sublimation of metals and stable compounds. Secondly, to apply the so-called 'third-law method', widely used in thermochemistry of equilibrium reactions, to the calculation of the E parameters in kinetic investigations of free-surface solid decompositions. Both these goals are connected through the interrelationship between the T and E parameters.

2. Theoretical

2.1. Basic thermodynamic relations

From the basic equation of chemical thermodynamics,

$$RT \ln K_P = T\,\Delta S_T^\circ - \Delta H_T^\circ \tag{1}$$

where R is the gas constant, T the absolute temperature, K_P the equilibrium constant, and ΔS_T° and ΔH_T° are the entropy and enthalpy changes for the process of any equilibrium reaction, we can obtain

$$\frac{T}{\Delta H_T^\circ} = \frac{1}{\Delta S_T^\circ - R \ln K_P} \tag{2}$$

In the case of the sublimation or evaporation of substance A (solid or liquid)

$$\mathrm{A(s/l)} = \mathrm{A(g)} \tag{3}$$

when K_P is equal to the equilibrium partial pressure, P_{A}; Eq. (2) may be rewritten as

$$\frac{T}{\Delta H_T^\circ} = \frac{1}{\Delta S_T^\circ - R \ln P_{\mathrm{A}}} \tag{4}$$

Eq. (4) can be applied to the estimation of temperature or enthalpy value in the process of evaporation or sublimation of any material for the known magnitude of one of these parameters, the appropriately defined value of P_{A} and the average value of ΔS_T°. In this respect, relationship (4) can be considered as a generalization of the well-known Trouton's rule relating the boiling temperature (T_{b}) and the molar enthalpy of vaporization (ΔH_T°) of liquids (see, e.g. [11]). At the boiling point, when $P_{\mathrm{A}} = 1$ bar, the average value of ΔS_T° (for a majority of liquids) is about $86 \pm 20\ \mathrm{J\,mol^{-1}\,K^{-1}}$ [11] and, as a result, $T_{\mathrm{b}}/\Delta H_T^\circ$ ranges from 9.4 to 15.2 $\mathrm{K\,mol\,kJ^{-1}}$ (the mean value: 11.6 $\mathrm{K\,mol\,kJ^{-1}}$).

In the case of sublimation of solids at rather low values of P_{A}, the relative deviation of $T_{\mathrm{sub}}/\Delta H_T^\circ$ values from the mean should be smaller because of the presence of the additional positive item ($-R \ln P_{\mathrm{A}}$) in the denominator of Eq. (4). To illustrate this conclusion, we present in Table 1 the corresponding parameters for 37 different substances. The list of substances includes some elements and stable binary compounds which sublime in accordance with equilibrium [9]. The temperatures of sublimation range from 180 K for ice to 3020 K for tungsten. At $P_{\mathrm{A}} = 10^{-7}$ bar (this magnitude corresponds to the initial sublimation temperatures, as will be discussed below), the mean values of $\Delta S_T^\circ = 144 \pm 17\ \mathrm{J\,mol^{-1}\,K^{-1}}$ (S.D.) and $T_{\mathrm{sub}}/\Delta H_T^\circ = 3.62 \pm 0.22\ \mathrm{K\,mol\,kJ^{-1}}$ (S.D.). The maximum relative deviation of $T_{\mathrm{sub}}/\Delta H_T^\circ$ ratio from the mean in the last case is less than half ($\pm 11\%$ compared to $\pm 25\%$ at the boiling point).

2.2. The second- and third-law methods for the calculation of ΔH_T°

Two different methods are used for the calculation of enthalpy values from thermal studies of equilibrium reactions, in particular, evaporation/sublimation processes. The so-called 'second-law' method is based on the application of the van't Hoff and Clausius–Clapeyron equations:

$$\frac{\mathrm{d} \ln K_P}{\mathrm{d}T} = \frac{\Delta H_T^\circ}{RT^2} \tag{5}$$

and

$$\frac{\mathrm{d} \ln P}{\mathrm{d}T} = \frac{\Delta H_T^\circ}{RT^2} \tag{6}$$

Table 1
$T_{\mathrm{sub}}/\Delta H_T^\circ$ ratio for sublimation of free elements and simple substances[a]

Reactant	ΔS_T° (J mol^{-1} K^{-1})	T_{sub} (K)	ΔH_T° (kJ mol^{-1})	$T_{\mathrm{sub}}/\Delta H_T^\circ$ (K mol kJ^{-1})
Ag	121.9	1089	279.4	3.90
B	144.9	2003	558.6	3.59
Be	123.5	1245	320.7	3.88
Cd	114.5	447	111.2	4.02
Co	136.1	1535	414.7	3.70
Cr	138.5	1419	386.6	3.67
Cu	124.0	1277	330.8	3.86
Fe	131.0	1502	398.0	3.77
Mo	143.9	2340	650.2	3.60
Ni	139.6	1527	417.7	3.66
Pd	118.2	1443	364.0	3.96
Pt	141.4	2005	554.3	3.62
Rh	148.5	1929	544.9	3.54
Ru	147.3	2311	650.0	3.56
Si	143.1	1602	443.8	3.61
Ti	133.2	1711	457.3	3.74
W	150.2	3020	858.3	3.52
Zn	115.1	517	128.7	4.02
$2\mathrm{I} \rightarrow \mathrm{I}_2$	151.0	223	63.5	3.51
$2\mathrm{Te} \rightarrow \mathrm{Te}_2$	154.8	558	161.2	3.46
KCl	139.4	779	213.0	3.66
KI	137.0	714	193.5	3.69
LiF	145.2	951	265.4	3.58
NaCl	140.7	804	220.8	3.64
$\mathrm{BaF_2}$	165.2	1229	367.6	3.34
$\mathrm{BeF_2}$	160.5	759	223.6	3.39
$\mathrm{CaF_2}$	176.3	1316	408.3	3.22
$\mathrm{HgBr_2}$	131.9	316	84.1	3.76
$\mathrm{HgCl_2}$	148.7	281	79.4	3.54
$\mathrm{HgI_2}$	144.8	321	89.5	3.59
$\mathrm{H_2O}$	144.2	180	50.0	3.60
$\mathrm{MgF_2}$	167.3	1235	372.0	3.32
$\mathrm{SnCl_2}$	164.2	429	127.8	3.36
$\mathrm{SrF_2}$	167.1	1359	409.2	3.32
$\mathrm{ThO_2}$	173.0	2358	723.9	3.26
$\mathrm{ZrO_2}$	168.5	2418	731.4	3.31
$4\mathrm{P(white)} \rightarrow \mathrm{P_4}$	115.2	236	58.9	4.01
Average ± S.D.	144 ± 17			3.62 ± 0.22

[a] T_{sub} corresponds to the vapor partial pressure of 10^{-7} bar.

After integration of Eq. (6), valid for evaporation/sublimation processes, we receive

$$R\ln P = -\frac{\Delta H_T^\circ}{T} + \text{constant} \tag{7}$$

From measurements of P at several different temperatures, it is easy to obtain the ΔH_T° value (the slope of the plot in $R\ln P$ versus T^{-1} scale). The advantage of this method consists in the possibility of using any parameter that is proportional to the P-value, instead of absolute values of P. No values of thermodynamic functions are necessary for the calculations.

The so-called third-law method is based on the direct application of Eq. (1) or the equivalent equation valid for simple evaporation/sublimation processes:

$$\Delta H_T^\circ = T(\Delta S_T^\circ - R\ln P) \tag{8}$$

In this case, a measurement at only one temperature is sufficient for the determination of ΔH_T° but a knowledge of absolute values of the entropies of all components in the reaction is necessary for the calculation. These values are available now for the majority of substances [12–15]. As can be seen from the analysis of results reported in [12,16] for several tens of substances, the data calculated by the third-law method are in general the order of magnitude more precise than those calculated by the second-law method. This is mainly connected with the systematic and random errors in the determination of the true temperature of reactant. It is clear if we compare Eq. (8) with Eq. (6) rewritten as follows:

$$\Delta H_T^\circ = R\frac{\mathrm{d}\ln P}{\mathrm{d}\,(1/T)} \qquad (9)$$

Instead of a proportional dependence of the error in ΔH_T° determination on the error of T in the case of the third-law method, the error in ΔH_T° determination is proportional to the error in the slope of the plot in the case of the second-law method.

Eq. (9) can be presented in the form

$$\Delta H_T^\circ = \frac{T_{\max} - T_{\min}}{T_{\max}T_{\min}} R \ln \frac{P_{\max}}{P_{\min}} \qquad (10)$$

where $P_{\max}$ and $P_{\min}$ are the partial pressures at the maximum ($T_{\max}$) and minimum ($T_{\min}$) temperatures of the experiment. It can be seen that the error in $T_{\max}$ determination (for example, because of the self-cooling effect) results in much higher error in ΔH_T° calculation in case of the second-law method. For illustration, at $T_{\min} = 900$ K and $T_{\max} = 1000$ K, the error in 10 K ($T_{\max} = 990$ K) results in the error in ΔH_T° calculation about 9% instead of only 1% in case of the third-law method applied at $T_{\max}$.

3. Results and discussion

3.1. The ratio of the initial temperature to the E parameter for decomposition reactions

It has been shown above (Section 2.1) that, for equilibrium sublimation reactions, the criterion $T_{\mathrm{sub}}/\Delta H_T^\circ = 3.62 \pm 0.22$ K mol kJ^{-1} (S.D.) is valid, where the value of T_{sub} corresponds to the partial vapor pressure of 10^{-7} bar. If to accept that, in line with the physical approach [9], all decomposition reactions proceed in accordance with the equilibrium laws (but with the formation of primary gaseous products which may differ of those at equilibrium), then it should be expected that the above criterion is valid for these reactions also. In Tables 2 and 3, we present the corresponding data from the available literature [5,17–71]. Table 2 contains the results for the decompositions of 50 substances into gaseous products only and Table 3 for the decompositions of 50 compounds into gaseous and solid (after the condensation of primary low-volatility gaseous species) products. Instead of T_{sub}, the value of the initial decomposition temperature, T_{in}, was used. It happened that for different instrumental techniques and different experimental conditions used in kinetic investigations, the reported initial temperatures of decomposition correspond, with rare exceptions, to the partial pressure of gaseous products of about 10^{-7} bar (within of factor of 10 in both directions). This item has been discussed in detail for gravimetry [9,10], ET AAS [5,6] and quadrupole mass-spectrometry (QMS) [56,72]. In line with the physical approach [9], the E parameters (or specific enthalpies) from the Arrhenius equation, which are reported in the same publications, were used instead of ΔH_T° values.

The majority of results included in Tables 2 and 3 were obtained under isothermal conditions. The exceptions were only for the results obtained by ET AAS and QMS. In these cases, the mass of samples deposited on the surface of graphite heaters as a submonolayer (by drying of a drop of solution) was in the microgram range and the self-cooling effect could be neglected. In all cases, the experiments were performed in vacuum or an inert atmosphere, i.e. in the absence of primary gaseous products in the reactor (the equimolar mode of evaporation [5–10]). And finally, where there were several publications devoted to the same substance, preference was given to the results obtained by the most experienced groups of workers under the leadership of Searcy and Munir, Pavlyuchenko and Prodan, Fesenko and Bolgar, Topley, Jacobs, Galwey, Ingraham, Alcock and Okhotnikov. We included in these tables results for different types of substances: from some metalloids (As and Sb) and simple binary compounds (oxides, halogenides, nitrides, carbides and borides) to metal salts of inorganic and organic acids (nitrates, sulfates, carbonates,

Table 2
T_{in}/E ratio for decomposition of substances into gaseous products[a]

Reactant	Sample	Atmosphere	Method	T_{in} (K)	E (kJ mol^{-1})	(T_{in}/E) (K mol kJ^{-1})	Reference
As[b]	Crystal	Vacuum	I-G	550	183	3.01	[17]
Sb[b]	Crystal	Vacuum	I-G	650	207	3.14	[17]
Al_2O_3	Sml	Ar	NI-AAS	2100	638	3.29	[5]
BaO	Sml	Ar	NI-AAS	2200	468	4.70	[5]
BeO	Sml	Ar	NI-AAS	2200	600	3.67	[5]
Bi_2O_3	Sml	Ar	NI-AAS	1100	245	4.49	[5]
CaO	Sml	Ar	NI-AAS	2000	518	3.86	[5]
CdO	Sml	Ar	NI-AAS	800	233	3.43	[5]
Cr_2O_3	Sml	Ar	NI-AAS	1900	502	3.78	[5]
Ga_2O_3	Sml	Ar	NI-AAS	1500	427	3.51	[5]
HgO	Powder	Vacuum	I-G	650	193	3.36	[18]
In_2O_3	Sml	Ar	NI-AAS	1300	361	3.60	[5]
Li_2O	Sml	Ar	NI-AAS	1400	361	3.88	[5]
MgO	Sml	Ar	NI-AAS	1800	504	3.57	[5]
MnO	Sml	Ar	NI-AAS	1700	450	3.78	[5]
PbO	Sml	Ar	NI-AAS	1100	240	4.58	[5]
SrO	Sml	Ar	NI-AAS	2100	500	4.20	[5]
V_2O_3	Sml	Ar	NI-AAS	2200	633	3.48	[5]
ZnO	Crystal	Vacuum	I-T	1400	397	3.53	[19]
GeO_2	Powder	Vacuum	I-MS	1213	341	3.56	[20]
SiO_2	Powder	Vacuum	I-MS	1773	508	3.49	[21]
SnO_2	Pellet	Vacuum	I-G	1239	348	3.56	[22]
CdS	Crystal	Vacuum	I-G	882	238	3.71	[23]
CdSe	Crystal	Vacuum	I-G	957	236	4.06	[24]
ZnS	Crystal	Vacuum	I-T	998	258	3.87	[25]
ZnSe	Crystal	Vacuum	I-T	952	294	3.24	[26]
AlN	Pellet	Vacuum	I-G	1590	542	2.93	[27]
GaN	Crystal	Vacuum	I-T	1166	305	3.82	[28]
InN	Crystal	Vacuum	I-QMS	1020	336	3.04	[29]
UN	Powder	Vacuum	I-R	1873	526	3.56	[30], p. 191
Be_3N_2	Pellet	Vacuum	I-G	1610	428	3.76	[31]
Mg_3N_2	Pellet	Vacuum	I-T	1000	238	4.20	[32]
KN_3	Crystal	Vacuum	I-G	513	144	3.56	[33], p. 238
NaN_3	Crystal	Vacuum	I-G	495	151	3.28	[33], p. 238
TiN	Powder	Vacuum	I-G	1987	533	3.73	[34], p. 167
ZrN	Powder	Vacuum	I-G	2236	667	3.35	[34], p. 169
HfC	Pellet	Vacuum	I-G	2773	778	3.56	[30], p. 187
TaC	Pellet	Vacuum	I-G	2973	955	3.11	[30], p. 188
ThC_2	Powder	Vacuum	I-R	2673	708	3.78	[34], p. 113
ZrC	Pellet	Vacuum	I-G	2773	831	3.34	[34], p. 86
LaB_6	Pellet	Vacuum	I-MS	1993	561	3.55	[30], p. 181
SrB_6	Pellet	Vacuum	I-M	1773	410	4.32	[30], p. 181
ZrB_2	Pellet	Vacuum	I-G	2173	640	3.40	[35]
$BaSO_4$	Crystal	Vacuum	I-T	1422	384	3.70	[36]
HgC_2O_4	Powder	Vacuum	I-G	373	110	3.39	[37]
NH_4HCO_3	Pellet	Vacuum	I-G	293	80	3.66	[38], p. 431
NH_4ClO_4	Pellet	N_2 (reduced)	I-M	653	162	4.03	[39]
$CH_2(COOH)_2$	Liquid	Air	I-M	407	136	2.99	[33], p. 262
Tetryl	Liquid	Air	I-M	484	161	3.01	[33], p. 259
$NH_3{\cdot}NI_3$	Powder	Vacuum	I-G	253	79	3.20	[33], p. 243

[a] Sml: sub-monolayer; I: isothermal; NI: non-isothermal; G: gravimetric; T: torsion; M: manometric; R: radioactivity; MS: mass spectrometry.

[b] As and Sb sublimate in accordance with the stoihiometry: $6M \rightarrow M_4 + M_2$ (see Table 4).

Table 3
T_{in}/E ratio for decomposition of compounds into gaseous and solid (eventual) products[a]

Reactant	Sample	Atmosphere	Method	T_{in} (K)	E (kJ mol^{-1})	(T_{in}/E) (K mol kJ^{-1})	Reference
Ag_2O	Powder	Vacuum	I-M	553	151	3.66	[40]
Cu_2O	Powder	Vacuum	I-G	900	205	4.39	[41]
FeO	Powder	Vacuum	I-G	1270	331	3.84	[42]
NiO	Powder	Ar	I-G	1180	305	3.87	[43]
Pb_3O_4	powder	vacuum	I-G	731	188	3.89	[44]
AgN_3	Pellet	N_2 (reduced)	I-M	503	151	3.33	[45]
PbN_6	Powder	Vacuum	I-M	468	152	3.08	[46]
TlN_3	Crystal	Vacuum	I-M	513	149	3.44	[47]
Ag_2CO_3	Powder	Vacuum	I-G	420	96	4.38	[48]
$CdCO_3$	Powder	Vacuum	I-G	513	151	3.40	[49]
$ZnCO_3$	Powder	Vacuum	I-G	523	159	3.29	[50]
$MgCO_3$	Powder	Vacuum	I-G	714	192	3.72	[51]
$CaMg(CO_3)_2$	Crystal	Vacuum	I-T	824	195	4.23	[52]
$CaCO_3$	Crystal	Vacuum	I-G	934	220	4.25	[53]
$SrCO_3$	Powder	Vacuum	I-G	888	290	3.06	[54]
$BaCO_3$	Powder	Vacuum	I-G	1215	283	4.29	[55]
$NaHCO_3$	Powder	N_2	I-G	383	109	3.51	[38], p. 359
$AgNO_3$	Sml	Vacuum	NI-QMS	580	167	3.47	[56]
$Cd(NO_3)_2$	Sml	Vacuum	NI-QMS	622	183	3.40	[56]
$Pb(NO_3)_2$	Sml	Vacuum	NI-QMS	581	145	4.01	[56]
$Ca(NO_3)_2$	Powder	Vacuum	I-G	773	229	3.38	[57]
$Al_2(SO_4)_3$	Pellet	N_2	I-G	923	268	3.44	[58]
$BeSO_4$	Powder	O_2	I-G	875	217	4.03	[38], p. 405
$CdSO_4$	Powder	N_2	I-G	1035	289	3.58	[59]
$CoSO_4$	Powder	Air	I-G	1113	315	3.53	[60]
$CuSO_4$	Powder	Air	I-G	963	262	3.68	[38], p. 407
$FeSO_4$	Powder	Air	I-G	949	253	3.75	[38], p. 406
$MgSO_4$	Powder	Air	I-G	1193	312	3.82	[61]
$NiSO_4$	Pellet	N_2	I-G	1033	257	4.02	[62]
UO_2SO_4	Powder	He	I-G	912	245	3.72	[38], p. 408
$CsMnO_4$	Crystal	Vacuum	I-G	513	141	3.64	[38], p. 386
$KMnO_4$	Crystal	Vacuum	I-G	489	165	2.96	[63]
$NaMnO_4$	Crystal	Vacuum	I-G	400	128	3.13	[38], p. 386
$Cu(HCOO)_2$	Powder	Vacuum	I-G	430	146	2.95	[38], p. 445
$Th(HCOO)_4$	Powder	Ar	I-G	498	150	3.32	[38], p. 446
$UO_2(HCOO)_2$	Powder	Ar	I-G	538	169	3.18	[38], p. 446
$Ni(CH_3COO)_2$	Powder	Vacuum	I-G	548	150	3.65	[38], p. 449
$Ag_2C_2O_4$	Powder	Vacuum	I-G	378	113	3.35	[64]
CuC_2O_4	Powder	Vacuum	I-M	521	136	3.83	[65]
MnC_2O_4	Powder	Vacuum	I-G	608	180	3.38	[66]
NiC_2O_4	Powder	Vacuum	I-G	503	159	3.16	[67]
PbC_2O_4	Powder	Vacuum	I-G	582	151	3.85	[68]
$Mg(OH)_2$	Crystal	Vacuum	I-G	550	126	4.37	[69]
$KAl(Si_3Al)O_{10}(OH)_2$	Powder	Vacuum	I-G	818	225	3.64	[70], p. 215
$Li_2SO_4{\cdot}H_2O$	Crystal	Vacuum	I-QCM	300	87	3.45	[71]
Ba-styphnate·H_2O	Powder	vacuum	I-G	542	153	3.54	[38], p. 477
Pb-styphnate·H_2O	Powder	Vacuum	I-G	468	138	3.39	[38], p. 477
$BaCl_2{\cdot}2H_2O$	Crystal	N_2	I-PP	313	87	3.60	[70], p. 218
$MgC_2O_4{\cdot}2H_2O$	Crystal	N_2	I-G	425	111	3.83	[38], p. 247
$CuSO_4{\cdot}5H_2O$	Crystal	Vacuum	I-QCM	260	74	3.51	[70], p. 216

[a] Sml: sub-monolayer; I: isothermal; NI: non-isothermal; G: gravimetric; T: torsion; M: manometric; PP: periodic photomicrography; QCM: quartz crystal microbalance.

permanganates, formates, acetates and oxalates), and hydrated salts. Some explosive substances (azides, ammonium salts, tetryl, metal styphnates and nitrogen iodide) were included as well. The initial decomposition temperatures for these substances range from 253 K for nitrogen iodide to 2973 K for TaC.

As can be seen from the analysis of these results, the ratio T_{in}/E (K mol kJ^{-1}) in all cases is very close to the theoretical $T_{\mathrm{sub}}/\Delta H_T^\circ$ value: 3.62 ± 0.22 (S.D.). The mean value of T_{in}/E is equal to 3.61 ± 0.39 (S.D.) for the reactants in Table 2 and 3.62 ± 0.37 (S.D.) for the reactants in Table 3. We see that there is no difference between the mean T_{in}/E-values for reactants decomposed into gaseous products only and those ultimately decomposed to yield solid and gaseous products. The only difference between theoretical $T_{\mathrm{sub}}/\Delta H_T^\circ$ values (for the equilibrium sublimation) and experimental T_{in}/E-values is in their deviation from the mean magnitude (3.6). This is explained by random errors in the determination of E parameter and the uncertainty in the relation of reported initial temperatures of decomposition to the equivalent partial pressure of product vapor. (One would expect a much higher deviation than this). The distribution of T_{in}/E-values for all 100 reactants is shown in Fig. 1. Each point of this distribution was calculated within steps of equal increment (0.2) in T_{in}/E ratio. The distribution is rather close to the Gaussian curve. This supports a random origin of errors. If, in addition to these 100 reactants, to take into account the other data available in the literature (obtained under isothermal conditions and the equimolar mode of decomposition, with the use of contracting geometry models), the deviation of T_{in}/E-values from the mean might be increased but no more than 1.5–2 times. All the above strongly supports the equilibrium character of decomposition reactions which is the basic concept in the physical approach to the interpretation of kinetics of solid decompositions [9].

3.2. Calculation of the E parameter by the second- and third-law methods

All values of the E parameter reported in the literature up to the present time have been calculated exclusively by the second-law method or by its alternative based on the Arrhenius equation and Arrhenius-plots. In the last case, as discussed earlier (Section 2.2), any parameter proportional to the partial pressure of evolved gaseous product can be used: the rate constant, k, the flow of gaseous product, J, the mass change of reactant per time unit, $\Delta m/\Delta t$, atomic absorption or mass spectrometric signal, etc. We do not know of any purposeful use of the third-law method for the calculations of the E parameter. (The work by Munir and Mitchell [25] on the free-surface decomposition of ZnS with the rather high sublimation coefficient of about 0.3 is the exception. These workers used both methods). It is easy to understand. The application of the third-law method assumes the equilibrium, or close to equilibrium, advance of the process (as, for example, in the effusion experiments with the Knudsen cell or in the above-mentioned free-surface decomposition of ZnS). This condition was denied up to now in relation to free-surface solid decompositions as a whole. However, this is not the case. As shown above, all decomposition reactions proceed in accord with the equilibrium laws. This means that the third-law method can be used in all cases of decomposition. As has been shown earlier [8–10], the value of E parameter can be calculated

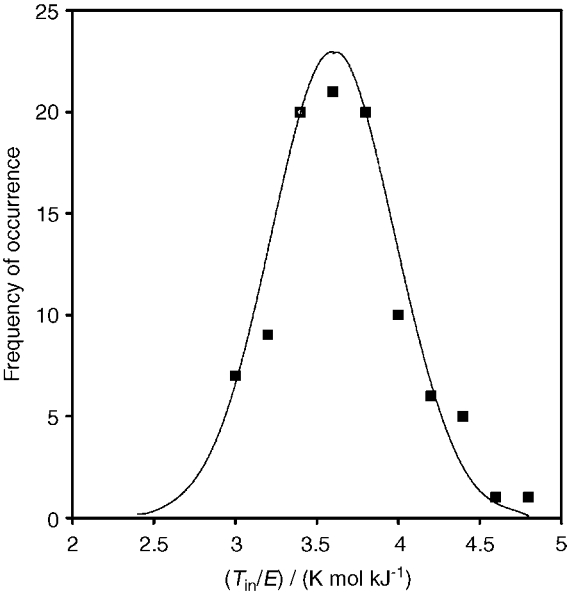

Fig. 1. The frequency of occurrence of T_{in}/E-values, presented in Tables 2 and 3, in steps of equal increment (0.2). A total of 100 values are included. The curve corresponds to the Gaussian distribution.

from the relationship:

$$E = T\left(\frac{\Delta S_T^\circ}{v} - R\ln P\right) \quad (11)$$

where P is the equivalent partial pressure referred to 1 mol of primary products and v is total number of moles of primary products.

To verify this conclusion, we applied this method to the calculation of the E parameter in the cases for which the available literature contained data on the absolute values of equivalent partial pressure of gaseous product(s). In all the selected works [17,19,21,23–28,31,32,52,59,73–77]: (i) the isothermal measurements were performed in high vacuum for the steady-state mode of decomposition and (ii) the samples used were crystals or pressed pellets with a known surface area. (These conditions are necessary for the correct application of the third-law method).

A list of the reactants with all necessary data, including the thermodynamic functions (ΔH_T° and ΔS_T°) for the implied decomposition reactions, is presented in Table 4. The composition of primary products for the implied reactions has been discussed in detail earlier [9,10,78]. Under the general heading of E parameter, we included several columns of data: the specific enthalpies ($\Delta H_T^\circ/v$) for the implied reactions and the E parameters calculated by the second- and third-law methods. In the last case, two values are indicated. The first corresponds to $\Delta S_T^\circ/v$ listed in this table, and second value, to the average magnitude of $\Delta S_T^\circ/v$ for these 20 reactants. (This value (147 J mol^{-1} K^{-1}) practically coincides with that (144 J mol^{-1} K^{-1}) for the reactants in Table 1). Except for the second-law data, reported in corresponding publications, all other data were calculated in this work.

The correlations between experimental values of the E parameter (E_{exp}) calculated by the second- or third-law methods, on the one hand, and its theoretical values ($E_{\mathrm{th}} = \Delta H_T^\circ/v$) for the implied reactions, on the other, are presented in Figs. 2–4, respectively. In case of the second-law method (Fig. 2), the correlation is very low ($r^2 = 0.75$, where r is the coefficient of linear correlation) and, in addition, strong systematic underestimating of experimental results is observed (for 13 out of 20 reactants). The mean value of relative standard deviation (R.S.D.) of experimental results from theoretical values is about 18%. The correlation represented in Figs. 3 and 4 for the third-law method is in dramatic contrast to this. The correlation in both cases is excellent ($r^2 = 0.997$ and 0.985) and no systematic deviation is observed. The mean value of R.S.D. is only 3 and 5%, respectively.

Several points here deserve more detailed discussion.

1. As can be seen from a comparison of the results obtained, the difference between precise and approximate versions of the third-law method is rather small. This means that, even in the absence of theoretical data on the entropy change for the decomposition reaction under investigation, the application of the third-law method is preferable (from the point of view of higher accuracy and precision).
2. The application of the third-law method at only one temperature greatly reduces (by a factor of 10 or more), the total time spent for the experiment in comparison with that for the second-law method. This is easy to understand by considering the total number of points usually used for plotting. For example, Searcy, Munir and their colleagues used from 10 to 60 points [19,22–25,28,31,32,36,52,75,76].
3. In contrast to the second-law method, the self-cooling effect in case of the third-law method results in overestimation of the calculated results. This is evident from Eq. (11). Therefore, it is preferable to use the result(s) of low-temperature measurements when the effect of self-cooling is minimal. On the other hand, from a comparison of results at different temperatures, the magnitude of self-cooling effect can be easily estimated.
4. From the reactants listed in Table 4, the alkaline-earth carbonates and $Li_2SO_4{\cdot}H_2O$ are the most popular substances used in kinetic studies. For all these reactants, the results obtained by the second-law method (even by the most experienced research workers) are 15–30% underestimated. This systematic error was discussed in detail earlier [9,10] and interpreted to be a consequence of the self-cooling effect. The present results obtained by the third-law method strongly support this explanation.
5. It is remarkable that for many binary compounds (GeO_2, CdSe, ZnS, AlN, GaN and Mg_3N_2) the molar quantities of primary atomic (O, Se, S and N)

Table 4

The *E* parameters for thermal decompositions of solids measured by the second- and third-law methods

Implied reaction[a]	v	T (K)	ΔH°_T (kJ mol^{-1})	ΔS°_T (J mol^{-1} K^{-1})	$(\Delta S^\circ_T/v)$ (J mol^{-1} K^{-1})	P_A (bar)	E (kJ mol^{-1})			Reference
							$(\Delta H^\circ_T/v)$	Second-law	Third-law[b]	
$6As \rightarrow As_4 + As_2$	2	550	353.9_{600}	314.5_{600}	157.3	6.6×10^{-10}	177	183	183/178	[17]
$6Sb \rightarrow Sb_4 + Sb_2$	2	650	429.0_{600}	305.8_{600}	152.9	1.3×10^{-9}	214	207	210/206	[17]
$SiO_2 \rightarrow 0.75SiO(g) + 0.25Si(g) + 1.25O$	2.25	1800	1242.3_{1800}	344.6_{1800}	153.2	8.0×10^{-9}	552	508	555/544	[21]
$GeO_2 \rightarrow GeO(g) + 0.25O_2 + 0.5O$	1.75	1313	650.2_{1300}	293.8_{1300}	167.9	8.5×10^{-7}	372	489	373/346	[59]
$SnO_2 \rightarrow SnO(g) + O$	2	1239	831.9_{1200}	321.4_{1200}	160.7	1.1×10^{-9}	416	351	412/395	[73]
$ZnO \rightarrow Zn(g) + O$	2	1400	724.5_{1400}	266.6_{1400}	133.3	2.5×10^{-7c}	362	384	364/383	[19]
$CdS \rightarrow Cd(g) + 0.35S_2 + 0.3S$	1.65	1000	391.8_{1000}	211.1_{1000}	128.0	2.6×10^{-6c}	237	238	235/254	[23]
$CdSe \rightarrow Cd(g) + 0.25Se_2 + 0.5Se$	1.75	1000	393.4_{1000}	216.9_{1000}	123.9	5.4×10^{-6}	225	234	225/248	[24]
$ZnS \rightarrow Zn(g) + 0.25S_2 + 0.5S$	1.75	1000	467.2_{1000}	230.8_{1000}	131.9	1.0×10^{-7}	267	258	266/281	[25]
$ZnSe \rightarrow Zn(g) + Se$	2	1000	516.4_{1000}	244.6_{1000}	122.3	1.7×10^{-7}	258	294	252/277	[26]
$BN \rightarrow B(g) + 0.5N_2$	1.5	1800	808.2_{1800}	232.1_{1800}	154.7	2.4×10^{-8}	539	329	541/527	[26]
$AlN \rightarrow Al(g) + 0.25N_2 + 0.5N$	1.75	1700	875.3_{1700}	257.5_{1700}	147.1	2.1×10^{-8}	500	542	500/500	[27]
$GaN \rightarrow Ga(g) + 0.25N_2 + 0.5N$	1.75	1200	620.3_{1200}	236.7_{1200}	135.3	1.4×10^{-8}	354	305	343/357	[28]
$Be_3N_2 \rightarrow 3Be(g) + 0.25N_2 + 1.5N$	4.75	1800	2225.5_{1800}	626.7_{1800}	131.9	1.5×10^{-7}	469	428	473/500	[31]
$Mg_3N_2 \rightarrow 3Mg(g) + 0.5N_2 + N$	4.5	1200	1356.7_{1200}	585.7_{1200}	130.1	1.3×10^{-6}	302	238	291/312	[32]
$MgCO_3 \rightarrow MgO(g)_{\downarrow} + CO_2$	2	500	415.9_{500}	355.0_{500}	177.5	1.6×10^{-14}	208	176	221/206	[74]
$CaMg(CO_3)_2 \rightarrow CaO(g)_{\downarrow} + MgO(g)_{\downarrow} + 2CO_2$	4	824	936.4_{900}	657.8_{900}	164.5	3.9×10^{-8}	234	192	252/238	[52]
$CaCO_3 \rightarrow CaO(g)_{\downarrow} + CO_2$	2	909	505.9_{900}	314.6_{900}	157.3	1.0×10^{-7}	253	205	265/255	[75]
$BaCO_3 \rightarrow BaO(g) + CO_2$	2	1163	638.7_{1200}	275.2_{1200}	137.6	4.5×10^{-8}	319	226	324/335	[76]
$Li_2SO_4{\cdot}H_2O \rightarrow Li_2SO_4(g)_{\downarrow} + H_2O(g)$	2	373	227.6_{298}	350.5_{298}	175.3	2.6×10^{-7}	114	85	112/102	[77]

[a] An arrow ($\downarrow$) implies taking into account one-half of condensation energy transfer to the reactant [9,10].

[b] First value corresponds to $\Delta S^\circ_T/v$ listed in this table, and second value, to the average magnitude of $\Delta S^\circ_T/v$ (147 J mol^{-1} K^{-1}).

[c] The averaged magnitude for opposite faces of wurtzite-type crystals.

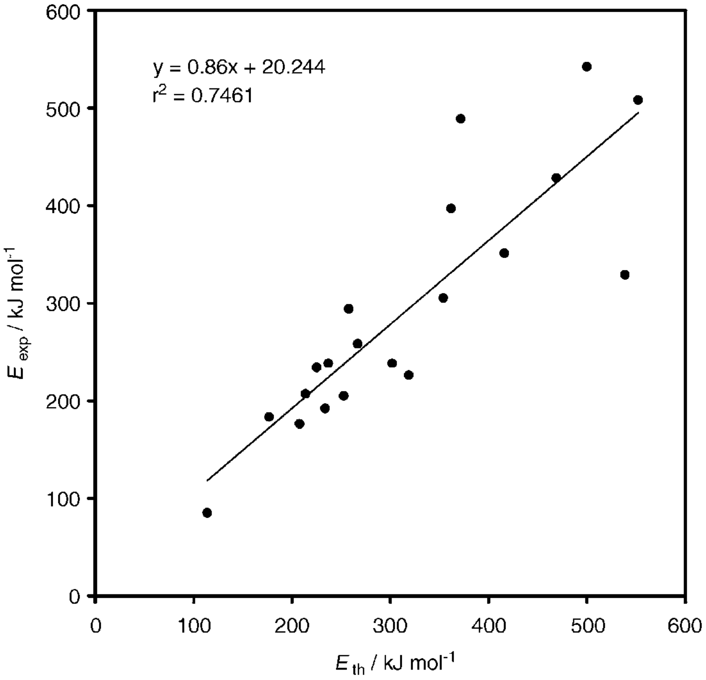

Fig. 2. Correlation of theoretical and experimental values of the E parameters, presented in Table 4. Experimental values were calculated by the second-law method.

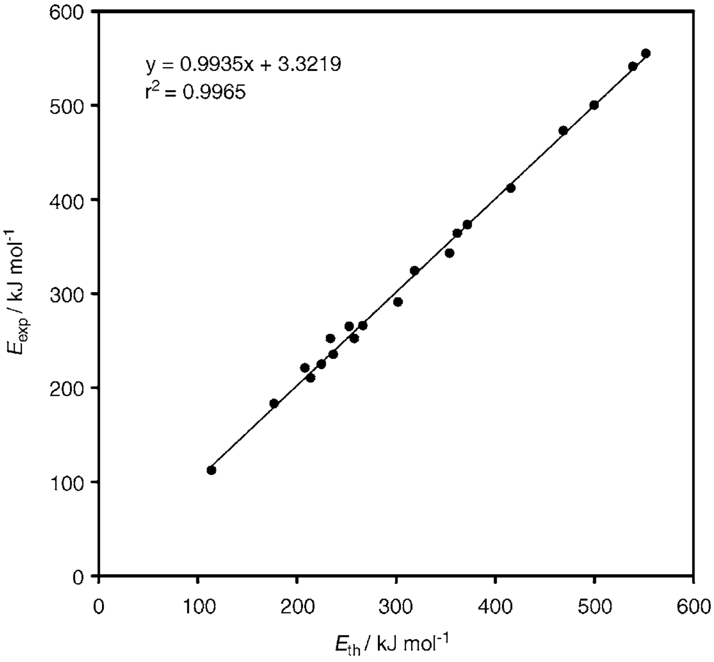

Fig. 3. Correlation of theoretical and experimental values of the E parameters, presented in Table 4. Experimental values were calculated by the third-law method taking into account the distinctive values of $\Delta S^{\circ}_{T}/v$ listed in Table 4.

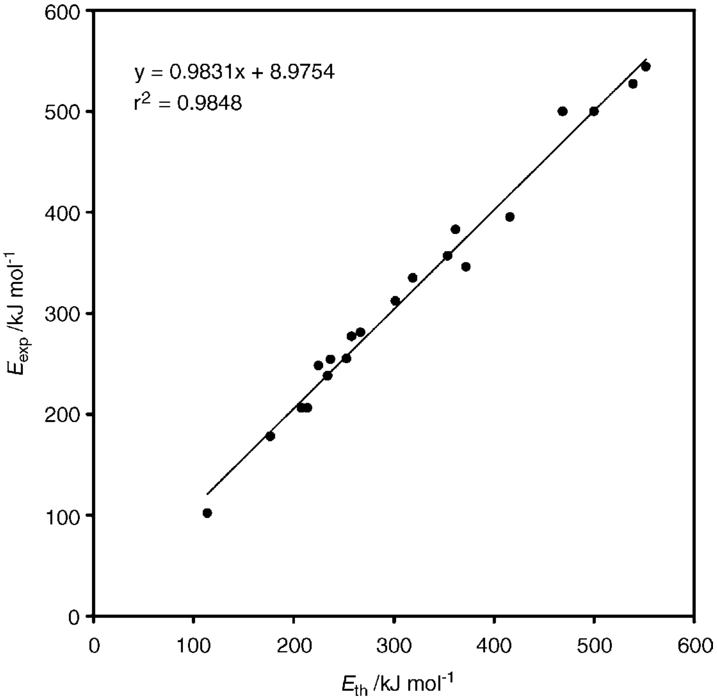

Fig. 4. Correlation of theoretical and experimental values of the E parameters, presented in Table 4. Experimental values were calculated by the third-law method taking into account the average value of $\Delta S^\circ_T/\nu = 147$ J mol^{-1} K^{-1}.

and molecular (O_2, Se_2, S_2 and N_2) species in the decomposition products relate as 2/1. This regularity deserves further study in relation to the crystallography of these compounds.

4. Conclusions

The following general conclusions can be made on the basis of this study.

1. A criterion of equilibrium development for the sublimation processes has been formulated and theoretically substantiated. It is based on the ratio of sublimation temperature, T_{sub} (which corresponds to the vapor partial pressure of 10^{-7} bar), to the enthalpy of sublimation, ΔH°_T. This ratio is in the range 3.6 ± 0.2 K mol kJ^{-1} (S.D.).
2. This criterion has been applied to the free-surface decompositions of 100 different substances including some metalloids and simple binary compounds together with metal salts of inorganic and organic acids, ammonium and hydrated salts. The experimental values of the initial temperature, T_{in}, and the E parameter, which are equivalent to the theoretical T_{sub} and ΔH°_T values, were taken from the literature. The mean value of T_{in}/E ratio for all reactants is equal to 3.6 ± 0.4 (S.D.). This means that the decomposition of all solids (irrespective of their composition and decomposition temperature) proceeds in agreement with the equilibrium laws. A higher deviation of T_{in}/E ratio from the mean (compared to theory) is connected with random errors in the determination of the E parameter and the uncertainty in the definition of the initial temperature of decomposition.
3. For the first time, the third-law method was used for the purposeful calculation of the E parameters in case of free-surface solid decompositions. The comparison of results obtained by the second- and third-law methods for 20 different reactants revealed the great advantages of the latter method in relation to reliability (precision and accuracy of determinations) and also to the time spent for the

experiment. (It is difficult to imagine how much effort, time and money have been spent in vain in the investigations of kinetics of solid decompositions because of neglecting this method).

It is hoped that the application of the physical approach to the interpretation of the decomposition kinetics, coupled with the new methodology of investigations based on the third-law method, will help to overcome the lingering stagnation in the field [79]. Many kinetic parameters reported in the literature need to be re-measured and re-considered in the framework of the physical approach. The primary goals on this way might be refinement of the decomposition kinetics for some traditional reactants (e.g. alkaline-earth carbonates and $Li_2SO_4{\cdot}H_2O$) and a more thorough investigation of the self-cooling effect responsible for a low reliability of the second-law and Arrhenius-plots methods. Such work (on the calcite decomposition) is now in progress.

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