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FUNDAMENTAL RESTRICTIONS OF THE SECOND-LAW AND ARRHENIUS PLOT METHODS USED IN THE DETERMINATION OF REACTION ENTHALPIES IN DECOMPOSITION KINETICS

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The apparent increase of the reaction enthalpy Δ*H* with temperature due to the self-cooling and condensation effects is responsible for the fundamental restrictions of the second-law and Arrhenius plot methods related to determination of this parameter. Theoretical analysis and a comparison with the experimental data indicate that the systematic underestimation of Δ*H* magnitudes determined by the second-law method equals 10–25% for the reactants decomposed to gaseous products and 15–50% for reactants decomposed to solids. Therefore, the use of these methods in decomposition kinetics is hardly acceptable. The replacement of the Arrhenius plot and second-law methods to the much more precise and accurate third-law method is desirable or even obligatory.

Keywords: *Arrhenius plot method, condensation effect, molar enthalpies, second-law method, self-cooling effect, third-law method*

Introduction

Three possible approaches to the investigation of kinetics and mechanisms of solid decompositions are known (Table 1). The first two (after Arrhenius and after Knudsen–Langmuir) in their final form were formulated in the 1960s, the last one (thermochemical), which has branched from the second approach, appeared in the 1980s. (To avoid possible confusion, it is necessary here to make a remark. The terminology used has undergone recently some changes or refinements. The terms 'physical approach', 'specific enthalpy' and 'specific entropy' introduced and used in previous communications of the author, have been replaced in the recent publications by 'thermochemical approach', 'molar enthalpy' and 'molar entropy'.) The apparent activation enthalpy Δ*H* (in the framework of the Knudsen–Langmuir approach to decomposition kinetics) and the activation energy *E* (in the framework of the Arrhenius approach) are usually determined by the use of the second-law and Arrhenius plot methods, respectively. Until recently, the third-law method, which has received wide recognition in equilibrium thermochemical studies, has not been used in kinetic investigations at all. The first publication on this subject in the framework of the thermochemical approach appeared only in 2002 [1]. Studies of L'vov and his colleagues still remain the only applications of this type (review papers [2, 3]). Theoretical and experimental analyses have shown that random errors in the determination of the reaction enthalpy Δ*H* with the third-law method are reduced by at least one order of magnitude compared with the two other methods. The purpose of the present work is to show that, in addition to the much reduced precision, there are other fundamental restrictions in the application of the second-law and Arrhenius plot methods to the determination of the Δ*H* or *E* parameters. (For simplicity, only the Δ*H* parameter will be mentioned in further discussion.)

Results and discussion

Because measurements by the third-law method are much more precise, it has become possible to confirm experimentally some quantitative conclusions that follow from the thermochemical approach to decomposition kinetics and to interpret some unusual effects observed [4, 5]. In addition, several new effects,

Table 1 Basics of the Arrhenius, Knudsen–Langmuir and thermochemical approaches (as applied to reactants decomposed to solids)

Constituent	Arrhenius approach	Knudsen–Langmuir approach	Thermochemical approach
Kinetics	Arrhenius equation	Hertz–Knudsen–Langmuir equation	Langmuir vaporization equations
Mechanism	Incongruent dissociative vaporization	Incongruent dissociative vaporization	Congruent dissociative vaporization
Methodology	Arrhenius plot method	Second-law method	Third-law method

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which were invisible in the framework of the Knudsen–Langmuir and Arrhenius approaches, have been revealed [4, 5]. One of these effects, namely, an increase of the enthalpies with temperature for reactants decomposed to solids is very important for analysis of the restrictions of the second-law and Arrhenius plot methods.

Indeed, the use of 'differential' (the second-law and Arrhenius plot) methods for determination of the reaction enthalpies is valid only if these quantities are kept constant for different temperatures. It is easy to show that the values of ΔH measured by the second-law method (ΔH^{II}) are related to those for the third-law method at the minimum and maximum temperatures of the experiments ($\Delta H^{\mathrm{III}}_{\min}$ and $\Delta H^{\mathrm{III}}_{\max}$) by the following equation [5], which is strictly valid if a small decrease of the entropy change with a temperature increase is neglected,

$$\Delta H^{\mathrm{II}}=\frac{\Delta H^{\mathrm{III}}_{\min}/T_{\min}-\Delta H^{\mathrm{III}}_{\max}/T_{\max}}{1/T_{\min}-1/T_{\max}} \qquad (1)$$

As can be seen, equality of the molar enthalpies determined by the second- and third-law methods ($\Delta H^{\mathrm{II}}=\Delta H^{\mathrm{III}}$) can be reached if $\Delta H^{\mathrm{III}}_{\min}=\Delta H^{\mathrm{III}}_{\max}$. If $\Delta H^{\mathrm{III}}_{\max}>\Delta H^{\mathrm{III}}_{\min}$, then $\Delta H^{\mathrm{II}}<\Delta H^{\mathrm{III}}_{\min}$. The ratio $\Delta H^{\mathrm{II}}/\Delta H^{\mathrm{III}}_{\min}$ is equal to

$$\Delta H^{\mathrm{II}}/\Delta H^{\mathrm{III}}_{\min}=\frac{1/T_{\min}-\Delta H^{\mathrm{III}}_{\max}/(\Delta H^{\mathrm{III}}_{\min}/T_{\max})}{1/T_{\min}-1/T_{\max}} \qquad (2)$$

If we assume, for example, that $T_{\max}/T_{\min}=1.25$ and $\Delta H^{\mathrm{III}}_{\max}/\Delta H^{\mathrm{III}}_{\min}=1.05$, then $\Delta H^{\mathrm{II}}/\Delta H^{\mathrm{III}}_{\min}=0.80$. A small increase of $\Delta H^{\mathrm{III}}_{\max}/\Delta H^{\mathrm{III}}_{\min}$ ratio is attended with much higher relative decrease of $\Delta H^{\mathrm{II}}/\Delta H^{\mathrm{III}}_{\min}$. This decrease rises with reduction in $T_{\max}/T_{\min}$ ratio. At $T_{\max}/T_{\min}=1.1$, the ratio $\Delta H^{\mathrm{II}}/\Delta H^{\mathrm{III}}_{\min}=0.50$.

These theoretical conclusions can be supported by the data taken from the literature (Table 2). The list of reactants in this table includes two groups of compounds, the first of which decompose to gaseous products only, and the second, yield both solid and gaseous products. These reactions were investigated in the works by Searcy *et al.* [6–12] and by Okhotnikov *et al.* [13–16]. (Both teams of workers belong to most experienced laboratories and there appears to be little doubt about reliability of their reported data.) All the experiments were performed in a high vacuum.

Table 2 lists the values of molar enthalpies for these reactions at the minimum and maximum temperatures of the experiments ($\Delta H^{\mathrm{III}}_{\min}/\nu$ and $\Delta H^{\mathrm{III}}_{\max}/\nu$), which we have calculated using the third-law method (ν is the number of moles of primary gaseous products), the molar enthalpies determined experimentally in the original works by the second-law method ($\Delta H^{\mathrm{II}}/\nu$) and the ratios $\Delta H^{\mathrm{II}}/\Delta H^{\mathrm{III}}_{\min}$. In addition, the values of $\Delta H^{\mathrm{II}}/\nu$ and $\Delta H^{\mathrm{II}}/\Delta H^{\mathrm{III}}_{\min}$, which calculated with Eqs (1) and (2), are presented.

Analysis of the data listed in Table 2 yields the following conclusions.

- The apparent difference between $\Delta H^{\mathrm{III}}_{\max}/\nu$ and $\Delta H^{\mathrm{III}}_{\min}/\nu$ for the first four reactants in Table 2, which decompose to gaseous products, is entirely due to self-cooling. By assuming that this effect is negligible at $T_{\min}$, one can estimate the temperature difference between the furnace and sample at $T_{\max}$. By the relationship $T_s/T_f=\Delta H^{\mathrm{III}}_{\min}/\Delta H^{\mathrm{III}}_{\max}$, it can be shown that the difference (T_f–T_s) varies from a few

Table 2 Impact of the self-cooling and condensation effects on the molar enthalpies determined by the second- and third-law methods

Decomposition reaction[a]	T/K		$(\Delta H^{\mathrm{III}}/\nu)$/ kJ mol^{-1}		$\Delta H^{\mathrm{III}}_{\max}/\Delta H^{\mathrm{III}}_{\min}$	$(\Delta H^{\mathrm{II}}/\nu)$/ kJ mol^{-1}		$\Delta H^{\mathrm{II}}/\Delta H^{\mathrm{III}}_{\min}$		Ref.
	Min.	Max.	Min.	Max.		expt.	calc.	expt.	calc.	
$Be_3N_2\leftrightarrow 3Be(g)+1.52N+0.24N_2$	1610	1880	486	493	1.014	428	444	0.88	0.91	[6]
$SnO_2\leftrightarrow SnO(g)+O$	1270	1485	411	418	1.017	351	370	0.86	0.90	[7]
$GaN\leftrightarrow Ga(g)+0.42N+0.29N_2$	1166	1428	356	366	1.028	305	311	0.86	0.87	[8]
$Mg_3N_2\leftrightarrow 3Mg(g)+1.52N+0.24N_2$	995	1330	304	329	1.083	223	230	0.73	0.76	[9]
$BaCO_3\leftrightarrow BaO(g)\downarrow+CO_2$	1076	1232	299	318	1.064	168	168	0.56	0.56	[10]
$CaCO_3\leftrightarrow CaO(g)\downarrow+CO_2$	909	1101	255	265	1.039	194	208	0.76	0.81	[11]
$0.5CaMg(CO_3)_2\leftrightarrow 0.5CaO(g)\downarrow+0.5MgO(g)\downarrow+CO_2$	824	900	246	258	1.049	116	116	0.47	0.47	[12]
$Li_2SO_4\cdot H_2O\leftrightarrow Li_2SO_4(g)\downarrow+H_2O$	348	433	104	115	1.106	50.6	59	0.49	0.57	[13]
$Li_2SO_4\cdot H_2O\leftrightarrow Li_2SO_4(g)\downarrow+H_2O$	315	363	108	112	1.037	84.9	82	0.79	0.76	[14]
$CaSO_4\cdot 2H_2O\leftrightarrow CaSO_4(g)\downarrow+2H_2O$	288	357	97.6	101	1.035	82.8	83	0.85	0.85	[15]
$CuSO_4\cdot 5H_2O\leftrightarrow CuSO_4(g)\downarrow+5H_2O$	255	303	88.0	89.8	1.020	74.5	78	0.85	0.89	[16]

[a] The reactions (in both groups) are arranged in order of decreasing temperature

Table 3 The molar enthalpies for several decomposition reactions calculated by the third-law method on the basis of primary data obtained by different workers

Decomposition reaction	T/K	$(\Delta H^{III}/\nu)$/ kJ mol^{-1}	Ref.	T/K	$(\Delta H^{III}/\nu)$/ kJ mol^{-1}	Ref.
$GaN\leftrightarrow Ga(g)+0.42N+0.29N_2$	1166	356	[8]	1260	361	[5, p. 176]
$Mg_3N_2\leftrightarrow 3Mg(g)+1.52N+0.24N_2$	1330	329^a	[9]	1232	337	[5, p. 176]
$BaCO_3\leftrightarrow BaO(g)\downarrow+CO_2$	1076	299	[10]	1077	300	[5, p. 214]
$CaCO_3\leftrightarrow CaO(g)\downarrow+CO_2$	1101	265^a	[11]	1215	265	[5, p. 215]
$0.5CaMg(CO_3)_2\leftrightarrow 0.5CaO(g)\downarrow+0.5MgO(g)\downarrow+CO_2$	824	246	[12]	820	254	[5, p. 216]
$Li_2SO_4\cdot H_2O\leftrightarrow Li_2SO_4(g)\downarrow+H_2O$	315	108	[14]	327	104	[5, p. 195]

^{a}At maximum temperatures of experiments

tens to one hundred degrees (namely, 26, 25, 39 and 101 K). One probable reason for the systematic increase of this difference might be a decrease of the heat transfer from the furnace to the sample by radiation at lower temperatures.

- The ratio $\Delta H^{III}_{max}/\Delta H^{III}_{min}$ for all the reactants in Table 2 varies in the range 1.01–1.10 (the average value is 1.045). At the same time, the ratio $\Delta H^{II}/\Delta H^{III}_{min}$ varies in the range 0.47–0.88 (the average value is 0.73). Therefore, a rather small increase of ΔH^{III} values with temperature produces a large decrease of ΔH^{II} values. The calculated values of $\Delta H^{II}/\nu$ and $\Delta H^{II}/\Delta H^{III}_{min}$ are in a good agreement with the experimental data. This result supports the validity of the correlation between ΔH^{II} and ΔH^{III} values described by Eq. (1).
- The ratios $\Delta H^{II}/\Delta H^{III}_{min}$ for the reactants decomposed to solid and gaseous products (the average magnitude is 0.68) are appreciably lower than those for the reactants decomposed to gaseous products only (the average magnitude is 0.83). This difference is related to the superposition of the condensation effect (an increase of the molar enthalpies with temperature for reactants decomposed to solids) on the self-cooling effect common for all the reactants. The systematic underestimation of molar enthalpies determined by the second-law methods equals 10–25% for the reactants decomposed to gaseous products and 15–50% for the reactants decomposed to solid and gaseous products. The value of such data, especially for solids that decompose to yield solid, if any, is very low. Therefore, the use of the second-law and Arrhenius plot methods in decomposition kinetics, without taking into account the above restrictions, is totally unjustified (especially in high-vacuum experiments when the heat transfer via radiation is the only method of sample heating). In this connection, the minor underestimation of molar enthalpies ($\Delta H^{II}/\nu$) in cases of low-temperature decompositions of $Li_2SO_4\cdot H_2O$, $CaSO_4\cdot 2H_2O$ and $CuSO_4\cdot 5H_2O$ can be explained by application of the special technique for improving the thermal contact between the crystal and the cylindrical holder: the lower and lateral surfaces of the crystal were coated with an In–Ga eutectic mixture [13–16]. As a result, the impact of self-cooling on the $\Delta H^{II}/\nu$ magnitudes was significantly reduced.

Table 3 contains the molar enthalpies for several decomposition reactions calculated by the third-law method in this work (Table 2) on the basis of primary data reported in [8–14] and the results, which were independently determined by L'vov and his colleagues [5]. For all reactants, the temperatures of experiments differ by not more than 100 K. From a comparison of these data, it can be seen that they are in excellent agreement: the relative difference in magnitudes of molar enthalpies measured in different works with different TA instrumentation is less than 4%. This is a good evidence of the reliability of the third-law method.

Conclusions

Theoretical study and analysis of experimental data reported in the literature indicate that systematic underestimations of the reaction enthalpies determined by the second-law method are usually 10–25% for the reactants decomposed to gaseous products and 15–50% for reactants with the formation of solids. In addition, as shown earlier [1–5], the precision of the second-law and the Arrhenius plot methods is at least one order of magnitude worse than that for the third-law method. Therefore, the replacement of the 'differential' (second-law and Arrhenius plot) methods to the 'absolute' third-law method in decomposition studies is desirable or even obligatory.

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