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DEPENDENCE OF THERMAL DECOMPOSITION RATE CONSTANT ON TEMPERATURE OF REACTION

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Abstract

On the basis of results of kinetic investigates of many compounds general temperature dependence of Gibbs free energy of activated complexes created in thermal decomposition processes and the reaction rate constant were calculated.

Keywords: kinetics of thermal decomposition, temperature dependence of Gibbs energy of activated complexes, temperature dependence of reaction rate constant, thermodynamic functions of activated complexes

Results and discussion

Kinetic parameters of thermal decomposition of particular compounds have been the subject of numerous publications. However, relationships between these parameters for different processes have not been described. The knowledge of these dependencies is very important in considerations of thermal stability and reactivity of solids.

Generally the kinetics of thermal decomposition of particular compounds is described by equation

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)f(\alpha) \qquad (1)$$

where α – is the degree of conversion, t – is the time, $k(T)$ – is the reaction rate constant at absolute temperature – T, R – is the gas constant. The rate constant may be expressed by the Arrhenius equation

$$k(T)=A\mathrm{e}^{-\mathrm{E/RT}} \qquad (2)$$

In this case the kinetics is characterised by three kinetic parameters: an apparent activation energy – E, a pre-exponential factor – A and a reaction model, $f(\alpha)$.

These kinetic parameters are very sensitive to conditions under which the reaction occurs and to the assumed mechanism of decomposition. Therefore, their comparison is very difficult, in particular, if they were obtained by different authors. This problem is very important in non-isothermal method of investigations.

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The activation energy does not define precisely [1] and it is not a function of state and its value depends on the way of reaction and weakly characterises these processes. Numbers of papers on the kinetic compensation effect have confirmed it [3–6].

The thermodynamic function, which well characterises the decomposition processes, is Gibbs free energy of activated complexes $-\Delta G^*$. It occurs in an equation on the reaction rate constant [2, 7]

$$k(T)=\frac{k_\mathrm{B}T}{h}\mathrm{e}^{-\Delta \mathrm{G}^*/\mathrm{RT}} \tag{3}$$

where k_B – Boltzmann constant, h – Planck constant.

It is the 'thermodynamic version' of the reaction rate constant. The Gibbs energy of activated complexes is a function which changes slowly with temperature for a given compound and characterises the decomposition process well.

In this work a great many results of kinetic investigations for different systems were analysed. Varied compounds about different properties and crystallographic structures, the decomposition temperatures of which ranged from 360 to 1235 K and Gibbs energy of transient states ranged from 106 to 396 kJ mol^{-1} were considered. Hydrates and anhydrous compounds, single and double salts, carbonates, sulphates, acetates of miscellaneous cations were among analysed compounds. The thermodynamic parameters of their activated complexes were calculated from Eyring equation after an analysis of kinetic data obtained at the Technical University of Szczecin by employing non-isothermal techniques (TG, DTG and DTA) [8–16]. The kinetic analysis was carried out by means of an integral method by applying the classical Coats–Redfern equation [17, 18]. The values of the thermodynamic function (the enthalpy – ΔH^* and entropy – ΔS^*) of activated complexes were calculated for different kinetic models [11] from the following dependencies [2]

$$\Delta H^*=E-RT_\mathrm{i} \tag{4}$$

$$\Delta S^*=R\left(\ln\frac{hA}{k_\mathrm{B}T_\mathrm{i}}-1\right) \tag{5}$$

$$\Delta G^*=\Delta H^*-T_\mathrm{i}\Delta S^* \tag{6}$$

The maximum reaction rates temperatures T_i were determined as the slope of $\Delta H^*(\Delta S^*)$ dependence Eq. (6) calculated from thermodynamic functions of activated complexes for different kinetic models. The values of Gibbs energy of particular activated complexes for analysed compounds were determined as an intercept of above dependence. The dependence of Gibbs free energy of activation complexes of different compounds on the maximum decomposition rate temperature is shown in Table 1 and in Fig. 1.

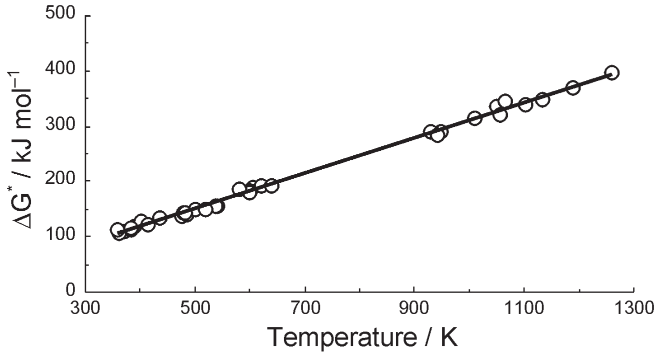

Fig. 1 The dependence of ΔG^* on the maximum reaction rate temperature – T_i

Table 1 Values of Gibbs free energy of activated complexes created in thermal decomposition

Compound	T_i/K	ΔG^*/ kJ mol^{-1}	Compound	T_i/K	ΔG^*/ kJ mol^{-1}
$BaCl_2 \cdot 2H_2O$	343	91	$Fe_2(SO_4)_3 \cdot 0.5H_2O$	537	155
$UO_2(CH_3COO)_2 \cdot 2H_2O$	358	113	$ZnSO_4 \cdot 0.8H_2O$	540	156
$ZnSO_4 \cdot 7H_2O$	362	106	$(NH_4)_2O \cdot 3V_2O_5$	582	186
$CuSO_4 \cdot 5H_2O$	370	109	$MgSO_4 \cdot H_2O$	598	180
$BaCl_2 \cdot H_2O$	377	100	$NiSO_4 \cdot H_2O$	607	189
$ZnSO_4 \cdot 6H_2O$	384	117	V_2O_5	622	193
$CoSO_4 \cdot 6H_2O$	384	114	$(CONH)_2$	638	191
$NiSO_4 \cdot 6H_2O$	390	120	$CuSO_4$	930	291
$CoSO_4 \cdot 4H_2O$	403	129	$Fe_2O(SO_4)_2$	943	284
$NiSO_4 \cdot H_2O$	607	189	$Fe_2(SO_4)_3$	947	290
$NiSO_4 \cdot 4H_2O$	437	135	$CuO \cdot CuSO_4$	1010	315
$CuSO_4 \cdot H_2O$	475	137	$CaCO_3$	1051	336
$Fe_2(SO_4)_3 \cdot 4.5H_2O$	478	144	$ZnSO_4$	1055	319
$CO(NH_2)_2$	483	144	$CaCO_3 \cdot MgCO_3$	1066	344
$(NH_4)_2O \cdot V_2O_5$	500	148	$ZnO \cdot ZnSO_4$	1134	348
$C_2O_2N_3H_5$	518	150	$CoSO_4$	1189	370

The relationship between the Gibbs energy of activation complexes in (kJ mol^{-1}) and their decomposition temperatures – T_i obtained on the basis of analysis of decomposition of 36 different compounds can be approximately described by the equation

$$\Delta G^* = 0.3184T_i - 8.24 \tag{7}$$

The value of determination of coefficient – R^2 is 0.9965.

The above relationship allows to express the dependence of the rate constant of thermal decomposition (s^{-1}) on the maximum reaction rate temperature in form of a function of one variable:

$$k=\frac{k_B T_i}{h}e^{-(0.3184\mathrm{T_i}-8.24)/\mathrm{RT_i}} \tag{8}$$

or

$$k=0.486\cdot10^{-7}T_i e^{991.1/\mathrm{T_i}} \tag{9}$$

Conclusions

On the basis of calculated values of Gibbs free energies of activated complexes created in 36 different thermal decomposition processes, the approximately dependence of the rate constant of analysed reactions (s^{-1}) on the maximum reaction rate temperature was described by the equation

$$k=0.486\cdot10^{-7}T_i e^{991.1/\mathrm{T_i}}$$

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