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O. P. MCHEDLOV-PETROSYAN, V. I. BABUSHKIN

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Abstract

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O. P. MCHEDLOV-PETROSYAN, V. I. BABUSHKIN

ON THE INTERRELATION BETWEEN THE THERMODYNAMICS AND KINETICS OF CERTAIN SOLID-PHASE REACTIONS

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Polanyi and Evans (^{1}) initiated a new direction in the study of the complex phenomena of interrelation between the kinetic and thermodynamic parameters of chemical reactions. They gave a theoretical justification for an approximate rule relating the magnitude of the activation barrier to the absolute value of the thermal effect ΔH for a series of reactions of the same type,

$$E = -\alpha \Delta H, \tag{1}$$

where E is the activation barrier, the same for the forward and reverse reactions, and they verified the validity of relation (1) using the interaction of a sodium atom with various halogen-substituted hydrocarbons as an example.

Subsequently this rule was confirmed by N. N. Semenov (^{2}) for a number of other chemical reactions of the same type in solutions.

In the present work an attempt is made to extend Polanyi' s concepts by establishing a connection between the activation energy of chemical reactions not only with their thermal effect, but also with the change in isobaric-isothermal potential, and at the same time to verify the correctness of these conclusions for reactions involving solids, which are of great importance for high-temperature chemistry.

Indeed, the connection between the activation energy and the isobaric-isothermal potential is readily established from the following premises.

Since

$$\Delta Z = -RT \ln K_p, \tag{2}$$

where K_p is the equilibrium constant ($K_p = k_1/k_2$), taking into account that the rate constants of the reaction k_1 and k_2 are exponentially dependent on the activation energy E,

$$k_1 = A_1 e^{-E/RT}, \tag{3}$$

we obtain

$$\Delta Z = -RT \ln\left(A_1 e^{-E_1/RT} / A_2 e^{-E_2/RT}\right),$$

or

$$\Delta E = \Delta Z + RT \ln(A_1/A_2), \tag{4}$$

where $\Delta E = E_1 - E_2$.

Thus, between ΔE and the change in the isobaric-isothermal potential of chemical reactions of the same type there also exists a rectilinear dependence, which makes it possible, from known thermodynamic data, to determine their kinetic characteristics. But the values of the coefficients A, even for reactions of the same type, may vary within considerable limits, which will affect the accuracy of the calculation results according to formula (4).

As an object for verifying the validity of the derived relation (4), we selected several types of solid-phase reactions: reactions of spinel formation (the system $MeO—R_2O_3$), reactions of orthosilicate formation (the system $2MeO—SiO_2$), and reactions of carbonate decomposition.

(system $MeCO_3$–MeO–CO_2). For all reactions, ΔH°_{298} and ΔZ°_{298} were calculated by the usual method. The initial thermochemical data and the values of the activation energies were taken from the reference literature ($^{3-8}$). The results of the calculations are summarized in Table 1, on the basis of which graphs were constructed for the dependence of the activation energy of the reactions considered on ΔH°_{298} and ΔZ°_{298}.

From these graphs the equations $E = f(\Delta H^0;\ \Delta Z^0)$ were derived (see Table 2).

Table 1

Reactions of the same type in the systems MeO–R_2O_3, $2MeO$–SiO_2, and $MeCO_3$–MeO–CO_2

No.	Reactions	ΔH^0_{298} from oxides, kcal/mol	ΔZ^0_{298} from oxides, kcal/mol	E experiment, kcal/mol	Source	E, determined from Figs. 1 and 2, kcal/mol
1	$MgO + Al_2O_3 = MgO \cdot Al_2O_3$	−5.0	−5.2	40.7	(6)	–
2	$MgO + Fe_2O_3 = MgO \cdot Fe_2O_3$	−3.6	−3.72	33.8	(6)	–
3	$MgO + Cr_2O_3 = MgO \cdot Cr_2O_3$	−5.0	−5.75	27.6	(6)	–
4	$FeO + Al_2O_3 = FeO \cdot Al_2O_3$	−2.3	−2.0	–	–	45.0$±6\|\|5\|*CaO+ Cr_2O_3*$ = CaO · Cr_2O_3
6	$CaO + Al_2O_3 = CaO \cdot Al_2O_3$	−2.5	−4.63	21.67	(8)	–
7	$FeO + Fe_2O_3 = FeO \cdot Fe_2O_3$	−7.7	−6.9	55.0	(6)	–
8	$SrO + Al_2O_3 = SrO \cdot Al_2O_3$	−2.0	−2.12	–	–	14$±6\|\|9\|*ZnO+ Fe_2O_3*$ = ZnO · Fe_2O_3

No.	Reactions	ΔH^0_{298} from oxides, kcal/mol	ΔZ^0_{298} from oxides, kcal/mol	E experiment, kcal/mol	Source	E, determined from Figs. 1 and 2, kcal/mol
11	$2CaO + SiO_2 = \beta\text{-}2CaO \cdot SiO_2$	–30.19	–30.64	23.2	(8)	–
12	$2FeO + SiO_2 = 2FeO \cdot SiO_2$	–8.4	–7.51	46.4	(6)	–
13	$2ZnO + SiO_2 = 2ZnO \cdot SiO_2$	–7.0	–6.88	–	–	–
14	$2MgO + SnO_2 = 2MgO \cdot SnO_2$	–	–	85.1	(6)	–
15	$2PbO + SiO_2 = 2PbO \cdot SiO_2$	–2.5	–2.8	114.0	(8)	–
16	$CaCO_3 = CaO + CO_2$	+42.5	+31.12	40.0	(7)	–
17	$Ag_2CO_3 = Ag_2O + CO_2$	+19.5	+7.63	20.4	(7)	–

No.	Reaction	ΔH^0_{298} from oxides, kcal/mol	ΔZ^0_{298} from oxides, kcal/mol	E experiment, kcal/mol	Source	E, determined from Figs. 1 and 2, kcal/mol
18	$MgCO_3$ = MgO + CO_2	+28.11	+15.61	26.0	(7)	–
19	$CdCO_3$ = CdO + CO_2	+23.79	+12.15	19.7	(7)	–
20	$MnCO_3$ = MnO + CO_2	+27.85	+14.34	22.5	(7)	–
21	$BaCO_3$ = BaO + CO_2	+63.85	+51.64	–	–	54\$±5||22|SrCO_3\$ = SrO + CO_2

The equations given in Table 2 make it possible to determine the activation energy from the values of ΔH^0 and ΔZ^0 for reactions of the same type (see Table 1).

Analysis of the equations in Table 2 shows that the relationship between the activation energy and the absolute values of the change in the isobaric-isothermal potential and of the heat effect is different for different types of reactions. Thus, for exothermic solid-phase nonequilibrium reactions of spinel formation, an increase in the absolute value of the heat effect and of the isobaric-isothermal potential is proportional to an increase in the activation energy (Fig. 1 A and B, straight lines 1).

Table 2

Reaction type	Equation
MeO + R_2O_3 = MeO R_2O_3	$E = 6.5\,\Delta H^0 \pm 6 E = -5.0 - 7.5\,\Delta Z^0 \pm 9$
2MeO + SiO_2 = 2MeO SiO_2	$E = 121 - 3.1\,\Delta H^0 E = 121 - 3.1\,\Delta Z^0$
$MeCO_3$ = MeO + CO_2	$E = 2.0 + 0.84\,\Delta H^0 \pm 2.5 E = 11.7 + 0.83\,\Delta Z^0 \pm 2.5$

As can be seen from the data of Table 1, the magnitude of the heat effect of most

Fig. 1

Figure 1: Fig. 1

spinel-formation reactions lies within the range 2–8 kcal/mol, and, consequently, for this type of reaction it will not exert a noticeable influence on the kinetics of the process.

For the same exothermic reactions in which the magnitude of the heat effect exceeds −15 kcal/mol, the direct dependence between the activation energy and the thermodynamic parameter may change to the inverse.

proportional (for example, in the reaction of formation of orthosilicates). In this connection, from the kinetic point of view, only those same-type reactions for which the values of ΔH^0 vary within definite limits can be regarded as truly same-type reactions. Thus, for example, the reactions of formation of $CaO \cdot Fe_2O_3$, $BaO \cdot Al_2O_3$, and $CaO \cdot B_2O_3$ will not obey the same regularities as those obeyed by the reactions of formation of spinels, since they belong to highly exothermic reactions (ΔH^0_{298} for them

Fig. 1. Relationship between the change in isobaric-isothermal potential (A), the thermal effect (B), and the activation energy of reactions in the following systems:
1 $-MeO—R_2O_3$; 2 $-2MeO—SiO_2$; 3 $-MeCO_3—MeO—CO_2$

is, respectively, −49.6; −24.0; −29.4 kcal/mole). In this connection we did not consider it possible, on the basis of the equations in Table 2, to determine for them the values of the activation energy.

Analysis of Fig. 1 shows that, for slightly exothermic reactions (with ΔH^0 up to 10 kcal/mole), the presence of a negative value of ΔZ^0 already at low temperatures ensures the thermodynamic probability of their occurrence, and the input of energy from outside is necessary to overcome the activation barrier associated with the loosening of the crystal lattice of the initial compounds and with ensuring the effective course of diffusion processes (see Fig. 1 A and B, straight lines 1). The small magnitude of the thermal effect in this case has no effect on reducing the activation energy.

In the case of reactions of formation of orthosilicates, we have an inversely proportional dependence between the activation energy and ΔH^0 and ΔZ^0, because significant values of the thermal effects (> 15 kcal/mole) begin to exert a considerable influence on lowering the activation energy. Thus, if for lead orthosilicate, at a thermal effect of −2.5 kcal/mole, E is equal to 114 kcal/mole, then for calcium orthosilicate, at $\Delta H^0_{298} = -30.64$ kcal/mole, $E = 23.2$ kcal/mole.

It is also characteristic that straight lines 1 and 2 (in Fig. 1) intersect at the point corresponding to approximately 15 kcal/mole. This circumstance once again emphasizes the fact that, upon reaching a magnitude of the thermal effect

15 kcal/mole, the exothermic effect begins to influence the kinetics of the reactions to a considerable extent. In this connection, the displacement of the point for iron orthosilicate is explained by the fact that ΔH^0_{298} for this reaction (−8.4 kcal/mole) does not reach the value −15 kcal/mole, and therefore it should with greater justification be assigned to the type of low-exothermic reactions.

Indeed, the point for iron orthosilicate ($\Delta H^0_{298} = -8.4$; $E = 46.4$), as well as that for zinc orthosilicate, fits very well on the line for spinel formation (Fig. 1, *B*, line 2).

As for the endothermic reactions of carbonate decomposition, all of them without exception at 298°K have a positive value of ΔZ^0_{298}, and for them an increase in temperature is necessary first of all in order that ΔZ become a negative quantity. In this connection, for endothermic reactions of carbonate decomposition the dependence between the activation energy and the thermal effect must be directly proportional. This proposition was fully confirmed (see Fig. 1, *A* and *B*, lines 3).

Thus, the theoretically established interrelation between activation energies and the thermodynamic parameters of reactions has received practical confirmation for three types of solid-phase reactions.

Further investigations in this direction may lead to still more important conclusions and open new possibilities in the study of chemical reactions.

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