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Abstract

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LATTICE ENERGY AND THE REACTIVITY OF SOLIDS

The study of the mechanism of reactions proceeding with the participation of solids is associated with great difficulties. Such reactions, in the overwhelming majority of cases, are accompanied by crystallization processes, which have been studied very little. The solids participating in reactions contain structural defects, not detectable by modern methods, which exert a great influence on the kinetics and mechanism of the reactions.

Despite the fact that the kinetics of solid-phase reactions has been studied for 50 years, the fundamental questions of the mechanism of their course remain unresolved to this day. Among such questions requiring solution are the mechanism leading to an increase in the reaction rate with time, the localization of the process at the interphase boundary, the influence of dispersion on the reactivity of solids, and others. Various points of view on the first two questions are considered in works ([1]). Up to the present time we have at our disposal entirely insufficient and contradictory experimental data and theoretical investigations on these questions.

The material presented in the present work makes it possible to gain a deeper understanding of the laws governing the internal mechanism of solid-phase reactions and to illuminate some of the questions posed.

Let us consider decomposition reactions of substances in the solid state in which a complex anion undergoes decomposition. These include salts of oxygen-containing inorganic acids, peroxides, polyhalide compounds, and many others.

The thermal effect of the reaction of formation of carbonates from a crystalline oxide and CO_2 is equal to

$$Q = -(U_{\mathrm{MeO}} - U_{\mathrm{MeCO3}}) + E_{\mathrm{CO3^{2-}}}, \tag{1}$$

where U_{MeO} and U_{MeCO3} are, respectively, the energies of the crystal lattices of the oxide and carbonate; $E_{\mathrm{CO3^{2-}}}$ is the energy of attachment of the oxygen ion to CO_2, which should practically not depend on the nature of the carbonate and oxide.

In the case of polyhalide compounds,

$$Q = -(U_{\mathrm{MeX}} - U_{\mathrm{MeX3}}) + E_{\mathrm{X3^{-}}}. \tag{2}$$

From the literature data (2) it is known that the activation energy of decomposition of certain carbonates is equal to the thermal effect. Consequently, the Arrhenius equation for these reactions can be written as

$$K = K_0 \exp\left\{-\frac{[-(U_{\mathrm{MeO}} - U_{\mathrm{MeCO3}}) + E_{\mathrm{CO3^{2-}}}]}{RT}\right\}. \tag{3}$$

In the case where the activation energy of carbonate formation is equal to q_1, we obtain

$$K = K_0 \exp\left\{-\frac{[-(U_{\mathrm{MeO}} - U_{\mathrm{MeCO3}}) + E_{\mathrm{CO3^{2-}}} + q_1]}{RT}\right\}. \tag{4}$$

Equations (3) and (4) clarify the physical meaning of the activation energy in the indicated decomposition reactions of solids. It is connected with the crystal-lattice energies of the disappearing and forming solids, as well as with the value $E_{\mathrm{CO3^{2-}}}$, which for all carbonates, if polarization energies are not taken into account, must have one and the same numerical value. If the reaction proceeds with the formation of stable intermediate products, this will introduce new terms into the exponential function of equation (4), without changing its physical meaning.

Analysis of equations (1), (3), and (4) makes it possible to solve a number of questions concerning the mechanism of solid-phase reactions. For this purpose it is necessary to know the lattice energy of the oxide, which is given in the literature (3), of the carbonates, and the affinity of the oxygen ion for CO_2. The lattice energy of the carbonates was calculated by us according to the formula of A. E. Fersman (4)

$$U = 256 \sum \; . \tag{5}$$

The values of for the cations and the CO_3 ion were taken from work (7). The energy of the crystal lattices of the oxides of the alkaline-earth metals, calculated by formula (5), is in good agreement with experimental data, which allowed us to apply this formula also for calculating the crystal-lattice energy of carbonates and sulfates. The heat effects of formation of carbonates from the metal oxide and CO_2 were taken or calculated from the data given in the handbook (5). Table 1 gives the results of calculations of the lattice energy and of the affinity of the oxygen ion for CO_2.

Table 1

Substance	$MgCO_3$	$CaCO_3$	$CdCO_3$	$BaCO_3$	$ZnCO_3$
U_{MeCO3}, kcal/mol	750.1	647.7	711.7	543.3	762.8
$E_{CO3^{2-}}$, kcal/mol	216.1	247.7	222.6	261.7	224.2

The mean value of the affinity energy of the oxygen ion for CO_2 is equal to 234.5 kcal/mol. Deviations from the mean are 4-11%. Knowing $E_{CO3^{2-}}$, one can find the value of the heat effect of the reaction of addition of CO_2 to MeO, and consequently also the activation energy of decomposition of carbonates for different degrees of dispersion of the initial solid substance and of the reaction product. From formula (1) we calculated the heat effects $Q_{m.d.}$ of the carbonate-formation reaction when the metal oxide and the carbonate are in the molecularly dispersed state*. The radius of the CO_3 ion was taken as equal to 2.85 Å ([6]). The results of the calculations are given in Table 2. For comparison, the values of the heat effects are given for reactions with substances in the crystalline state.

Table 2

Reaction product	$MgCO_3$	$CaCO_3$	$CdCO_3$	$BaCO_3$	$ZnCO_3$
Q_{cr}, kcal/mol	26.15	42.5	23.3	60	17
$Q_{m.d.}$, kcal/mol	122.5	161.9	–	1962	–

From the data of the table it follows that the heat effect of a reaction proceeding with substances in the molecularly dispersed state differs from the heat effect of a reaction with substances in the crystalline state.

In the case where the dispersion of one substance changes, while the dimensions of the crystals of the second substance are such that the binding energy of the ions does not depend on their number in the crystal, the heat effect of the reaction also changes.

If the salt is in the crystalline state and the binding energy of the ions in the crystal does not depend on their number, while the decomposition product—the metal oxide—is obtained in a highly dispersed state up to the formation of individual molecules, then the heat effect, and consequently also the activation energy—

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* The distances between ions were taken to be the same as in the crystal lattice, and the thermochemical radius of CO_3^{2-} is equal to 1.85 Å ([8]).

decomposition, as dispersion increases, increase substantially, and the reactivity of the carbonate decreases.

Thus, for example, in the decomposition of crystalline calcium carbonate and the formation of CaO in a molecularly dispersed state, the heat effect of the reaction is −405.8 kcal/mol. The reactivity of such a carbonate in the decomposition reaction will be very low. In the opposite case, when the carbonate is in a molecularly dispersed state and MeO crystals above the critical sizes are formed, the heat effect of the decomposition reaction is +201.4 kcal/mol, i.e., decomposition proceeds with the evolution of heat, and calcium carbonate under these conditions would have high reactivity.

Similar regularities with respect to dispersion and the heat effect of the reaction, the activation energy, and reactivity, as calculations of the heat effect of sulfate formation from MeO and SO_3, given in Table 3, show, are also observed in the case of decomposition and formation of sulfates. The thermochemical radius of the SO_4 ion, used for the calculations, is 2.3 Å (^{8}).

The affinity of SO_3 for the oxygen ion, calculated by the same formula (1) as the affinity of the oxygen ion for CO_2, for the reactions of formation of calcium sulfate is 312.4 kcal/mol, of barium sulfate −340.2 kcal/mol, and of magnesium sulfate −291.7 kcal/mol. The mean value is −314.7 kcal/mol*.

Table 3

	CaO_{cr} $CaSO_{4cr}$	BaO_{cr} $BaSO_{4cr}$	$CaO_{mol.\ disp.}$ $CaSO_{4mol.\ disp.}$	$BaO_{mol.\ disp.}$ $BaSO_{4mol.\ disp.}$	$CaO_{mol.\ disp.}$ $CaSO_{4cr}$	$BaO_{mol.\ disp.}$ $BaSO_{4cr}$	CaO_{cr} $CaSO_{4mol.\ disp.}$	BaO_{cr} $BaSO_{4mol.\ disp.}$
Q, kcal/mol	94.8	122.6	172.8	−225.9	450	435.7	−190.7	−91.8

Using formula (1), one can calculate the heat effect of a reaction when crystallites of different sizes participate in it and are formed. Reactivity, as follows from the data of Table 3, depends not only on the dispersion of the substance entering into the reaction, but also on the dispersion of the solid reaction product formed.

The large energy required to detach the oxygen ion from the CO_3 ion ($E_{CO_3^{2-}}$ = 234.5 kcal/mol) and from the SO_4 ion ($E_{SO_4^{2-}}$ = 314.7 kcal/mol), and the small activation energy show that the decomposition of complex anions, associated with the transfer of the oxygen ion and the formation of CO_2, takes place in a single act with a decrease in the distance between the ions (Me and O), and the energy expended on transfer is compensated by the energy released upon the approach of the metal and oxygen ions. Such an approach will lead to an increase in the interaction energy of the ions of the metal oxide molecule being formed with the lattice of the parent substance.

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REFERENCES

1. M. M. Pavlyuchenko, ZhFKh, **29**, No. 1, 39 (1955).

2. C. Slonim, *Zs. Elektrochem.*, **36**, 439 (1930); K. Fishbeck, Snaidt, *Zs. Electrochem.*, **38**, 199 (1932); W. Spencer, B. Topley, *J. Chem. Soc.*, **1928**, 2633.

3. A. F. Kapustinskii, ZhFKh, **5**, 59 (1934).

4. A. E. Fersman, *Selected Works*, 5, Publishing House of the Academy of Sciences of the USSR, 1959, p. 433.

5. V. V. Brykke, A. F. Kapustinskii, *Thermal Constants of Inorganic Substances*, Publishing House of the Academy of Sciences of the USSR, 1949.

6. Yu. V. Khodokov, *Elements of Electrostatic Chemistry*, Moscow, 1934.

7. G. B. Bokii, *Introduction to Crystal Chemistry*, Moscow State University Publishing House, 1954, p. 149.

8. K. B. Yatsimirskii, *Thermochemistry of Complex Compounds*, Publishing House of the Academy of Sciences of the USSR, 1951, p. 33.

* If the energy of the crystal lattices of carbonates and sulfates is calculated by Kapustinskii’ s structureless formula and the data obtained are used to calculate $E_{\mathrm{CO3}^{2-}}$ and $E_{\mathrm{SO4}^{2-}}$, then the following mean values are obtained: for $E_{\mathrm{CO3}^{2-}} = 212.6$ kcal/mol, for $E_{\mathrm{SO4}^{2-}} = 332.2$ kcal/mol. In calculating the energy, Goldschmidt radii of the cations and thermochemical radii of CO_3 and SO_4, equal to 1.85 and 2.3 (^{8}), were used.

Note: Figure translations are in progress. See original paper for figures.