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A THERMOANALYTICAL STUDY OF THE INTERACTION OF VANADIUMOXIDE(V) WITH CALCIUM OXIDE AND CALCIUM CARBONATE

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The interaction of V_2O_5 with calcium oxide and calcium carbonate was studied by thermal analysis. The results indicated that the macrosuccession of the phase transformations in the systems $CaO-V_2O_5$ and $CaCO_3-V_2O_5$ corresponds to an increasing calcium content in each successively formed calcium vanadate. Thermodynamical calculations carried out by methods available in the literature for determining the primary products and the succession of the subsequently formed products demonstrate that chemical reactions proceeding in the above systems are controlled by kinetic and not by thermodynamic factors.

The determination of the primarily formed compounds and of the succession of chemical transformations in oxide – salt systems appears as one of the most interesting and complex problems in inorganic chemistry, closely connected with the study of mass transfer, in particular, with the diffusion of ions. A complex thermal study, though bearing no unequivocal evidence of the direction of diffusion for a given particle, may none the less yield information on the stages of chemical processes in a complex system.

The present paper describes the thermoanalytical study of the succession of transformations in the systems $CaO - V_2O_5$ and $CaCO_3 - V_2O_5$, and the comparison of the results with the data of thermodynamic analysis.

In the system $CaO-V_2O_5$, according to the phase diagram [1], calcium metavanadate $Ca(VO_3)_2$ and calcium ortovanadate $Ca_3(VO_4)_2$ as well as pyrovanadate $Ca_2V_2O_7$ are formed. In recent years the vanadates $Ca_7V_4O_{17}$ [2], $Ca_4V_2O_9$ formed at 1250° [3] and $Ca_5V_2O_{10}$ obtained from a mixture of $CaCl_2$ and V_2O_5 at 700–1300° [4] were also synthetized.

Experimental

The starting compounds were analytical grade V_2O_5 and $CaCO_3$ and chemically pure grade CaO. In stoichiometric calculations including the latter we took into account the experimentally determined amounts of adsorbed CO_2 and water vapour, which were evolved subsequently in the course of thermal analysis and recorded on the corresponding curves. The samples were prepared by grinding the mixture of the components in a mortar in the presence of alcohol. The methods used in the study were thermal analysis (using the microthermoanalyzer Thermoflex manufactured by Rigaku, Japan, and the Derivatograph by MOM, Hungary) and X-ray diffractometry (using the diffractometer DRON-2 and CuK$_\alpha$ radition). The thermal treatment of the samples was carried out in pans ensuring good contact with the surrounding medium, sample mass was 300 to 500 mg, heating rate 5°/min when the derivatograph was used. With the Thermoflex microthermoanalyzer, the 10 – 50 mg samples were contained in crucibles and heating rate was 20°/min. The results in both cases complemented one another and led to analogous final conclusions. Parallely, other portions of the samples were heated in the derivatograph to the most characteristics temperatures shown by the thermal curves, for further X-ray studies. The lines in the diffraction patterns were identified using published data on calcium vanadates [2, 5, 6] and V_2O_5, CaO and $CaCO_3$ [7]. We limited the studies to compositions up to 75 mol-% CaO ($CaCO_3$).

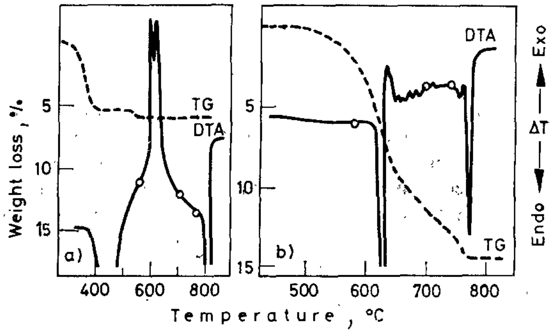

Fig. 1. Thermal curves of the mixtures $CaO-V_2O_5$ 1 : 1 (a) and $CaCO_3-V_2O_5$ 1 : 1 (b). Here and in Figures 2 and 3 the temperatures at which X-ray phase analysis of the samples were carried out are marked with small disks

The results of the experiments indicate that the interaction of V_2O_5 and CaO yielding $Ca(VO_3)_2$ starts at 500 – 520° and is accompanied by an important exothermic effect (Fig. 1a), on the background of which, at 620°, an endothermic effect is observed. The latter corresponds to the melting of the lowest-melting eutectic composition of the system $CaO-V_2O_5$ containing V_2O_5 and $Ca(VO_3)_2$. The reaction in the 1 : 1 ratio V_2O_5-CaO mixture ends in the temperature range of 700 to 760°. In the compact cake at 760° only calcium metavanadate was detected (Table 1) which melts, under decomposition, at 775°.

The chemical reaction between V_2O_5 and $CaCO_3$ (Fig. 1b) observed on the thermal curves by the mass loss of the sample, begins around 480°, that is, substantially below 630°, the temperature at which observable dissociation of the individual compound calcium carbonate starts. This finding, and also a comparison of the calculated activation energies [8] of the dissociation of $CaCO_3$ (43 – 48 kcal/mole) and the reaction of $CaCO_3$ with V_2O_5 yielding $Ca(VO_3)_2$ (20 – 30 kcal/mole) indicate that in the early period the starting components directly

Table 1

Change in the phase composition of the samples in the course of heating

Initial composition of sample	Temperature, °C	Phase composition
$CaO + V_2O_5$, 1 : 1	580	V_2O_5, CaO, $Ca(VO_3)_2$
	700	$Ca(VO_3)_2$
	760	$Ca(VO_3)_2$
$CaCO_3 + V_2O_5$, 1 : 1	580	V_2O_5, $CaCO_3$, $Ca(VO_3)_2$
	670	$Ca(VO_3)_2$, V_2O_5, $CaCO_3$
	725	$Ca(VO_3)_2$
$CaO + V_2O_5$, 2 : 1	550	V_2O_5, CaO, $Ca(VO_3)_2$
	640	$Ca(VO_3)_2$, $Ca_2V_2O_7$, CaO
	870	$Ca_2V_2O_7$
	920	$Ca_2V_2O_7$
$CaCO_3 + V_2O_5$, 2 : 1	586	V_2O_5, $CaCO_3$, $Ca(VO_3)_2$
	710	$Ca_2V_2O_7$, $Ca(VO_3)_2$, $CaCO_3$
	786	$Ca_2V_2O_7$
	950	$Ca_2V_2O_7$
$CaO + V_2O_5$, 3 : 1	540	V_2O_5, CaO, $Ca(VO_3)_2$
	645	$Ca(VO_3)_2$, $Ca_2V_2O_7$, CaO
	960	$Ca_2V_2O_7$, $Ca_3(VO_4)_2$
$CaCO_3 + V_2O_5$, 3 : 1	570	V_2O_5, $CaCO_3$, $Ca(VO_3)_2$
	690	$Ca_2V_2O_7$, $CaCO_3$
	810	$Ca_2V_2O_7$, $Ca_3(VO_4)_2$, $CaCO_3$
	970	$Ca_2V_2O_7$, $Ca_3(VO_4)_2$, CaO

react, without a previous dissociation of calcium carbonate taking place. According to thermochemical calculations [9] the interaction between the starting components forming calcium metavanadate is accompanied by a slight absorption of heat (10.15 kcal/mole).

The temperature 620° characterizes the appearance of the eutectic liquid phase indicated in the thermal curves by an endoeffect. An analysis of the TG curve allows to determine the amount of unreacted calcium carbonate, formed calcium metavanadate and free vanadium oxide in the moment when the system reaches this temperature, and also the ratio of the solid to liquid phase. According to the calculation the molar ratio $Ca(VO_3)_5$ to V_2O_5 is 1: 2.33. A comparison of this value with the ratio 1: 5.67, calculated from the phase diagram $CaO-V_2O_5$ in the eutectic point, indicates that the sample, at 620°, in addition to the eutectic melt, contains some unreacted $CaCO_3$ and $Ca(VO_3)_2$ crystals.

The mass ratio solid to liquid is 1: 1.4 in the sample in question, i.e. the amount of the liquid phase is substantially higher than that of the solid phase. As a result, the area of contact between the reacting substances increases, and their interaction is accelerated. On the other hand, the melt deteriorates the conditions of gas evolution from the surface of the reaction mixture and thereby decelerates the reaction. The resultant of these two processes defines the irregular, "broken" course of the DTA curve at 650 to 760°, which is characteristic for processes in which the gas phase (in the given case CO_2) bubbles through the melt.

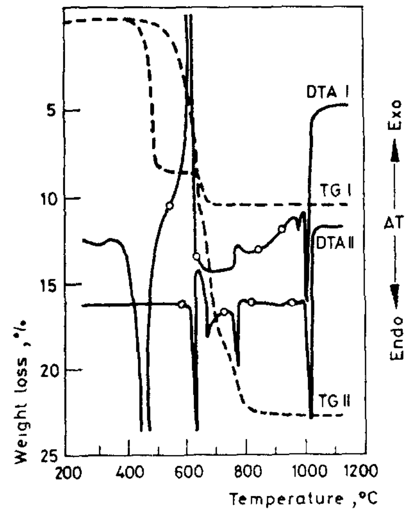

Fig. 2. Thermal curves of the mixtures $CaO—V_2O_5$ 2 : 1 (I) and $CaCO_3—V_2O_5$ 2 : 1 (II)

As a result of further heating and chemical reactions taking place, the amount of the liquid phase decreases, while the amount of calcium metavanadate increases. At temperatures preceding melting, the sample turns totally into a solid, mass loss due to CO_2 evolution stops, and X-ray analysis demonstrates the presence of $Ca(VO_3)_2$ only.

In the vanadium oxide and calcium oxide mixture with a molar ratio of 1 : 2 (Fig. 2), interaction at the temperature where the eutectic liquid phase appears becomes more intense, an important exothermic effect is recorded on the DTA curve, after which calcium metavanadate, pyrovanadate and calcium oxide are detected in the sample. Further heating results a small effect at 775° observed on the DTA curve, which corresponds to the melting of $Ca(VO_3)_2$, and at 920° the sample, a compact cake, consists of a single phase, namely calcium pyrovanadate, whose peritectic melting takes place at 975°.

In the interaction of vanadium oxide and calcium carbonate with a similar molar ratio, the mass loss up to the moment when the eutectic liquid phase appears affects the solid to liquid ratio assuming a value of 1 : 0.5 in this case. Hence the effect of the melt on the kinetics of the process will differ from that for the mixture containing 50 mol-% $CaCO_3$, and the character of the DTA curve over the temperature range of 620 to 775° will be different. The evolution of carbon dioxide is completed in the moment when calcium metavanadate melts, and this again promotes the completion of the reaction yielding calcium pyrovanadate.

With increasing contents of CaO and $CaCO_3$, resp., in the samples, the above successions of transformations are, in general lines, again observed. The effects recorded on the thermal curves (Fig. 3) correspond to the chemical interactions and subsequent melting of calcium meta-, pyro- and orthovanadates. It should, however, be observed that at high excesses of calcium oxide or calcium carbonate the formation of the primary product $Ca(VO_3)_2$ may be accompanied by the appearance of $Ca_2V_2O_7$, and at higher temperatures, $Ca_3(VO_4)_2$ may be formed besides calcium pyrovanadate. This is demonstrated both by the character of the thermal curves and by the data of X-ray phase analysis of samples heated to various temperatures.

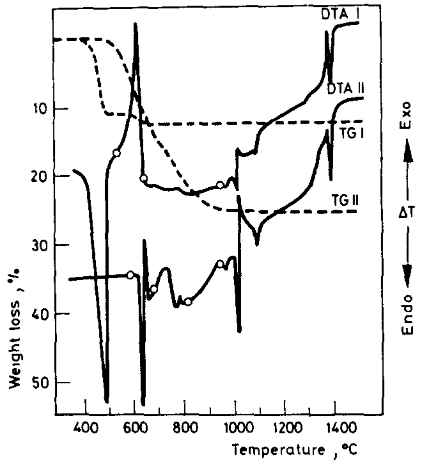

Fig. 3. Thermal curves of the mixtures $CaO—V_2O_5$ 3 : 1 (I) and $CaCO_3—V_2O_5$ 3 : 1 (II)

The results of the experiments allow to conclude that the interaction between vanadium oxide and calcium oxide or carbonate, resp., independently of the ratio of the components, starts in the solid-phase mixture and yields as primary reaction product calcium metavanadate. The recorded starting temperature of the reaction is also independent of the molar ratio, but differs for mixtures containing calcium oxide and carbonate, resp. The liquid phases formed by melting of both eutectics and individual compounds play an active part in the chemical reaction. Due to the presence of the liquid phase the area of contact between the reactants is increased and hence the reaction will be accelerated. Also, the equilibrium corresponding to the stoichiometric ratio of the components is established more rapidly in the liquid phase, which considerably distorts the exact succession of transformations taking place in the polycrystalline mixture. Under the chosen experimental conditions several chemical reactions simultaneously take place in mixtures rich in calcium. This is, however, in no contradiction to the major conclusion of the experimental part of this study, namely that the macrosuccession of phase transformations in the systems $CaO-V_2O_5$ and $CaCO_3-V_2O_5$ corresponds to an increase of the calcium content in each successive calcium vanadate being formed. The completion of the chemical transformations and the final equilibrium phase composition depend on the stoichiometric composition of the initial samples.

Thermodynamic analysis and discussion of results

Several approaches have been suggested in the literature for the assessment of the primarily formed products of interaction and of their succession in complex oxide–salt systems. (A bibliography on this problem is found particularly in the references [10–12].) Among the numerous – and partly contradictory – views let us mention the followings. The first compound being formed is (i) the most heat-resistant compound among all that can be formed in the system in question; (ii) the least heat-resistant compound; (iii) the compound closest to the eutectic mixture with the lowest melting point; (iv) the compound whose activation energy of formation is minimum as compared to the other possible compounds. The variety of factors specified as controlling the direction and succession of chemical transformations in complex heterogeneous systems, and in particular, defining

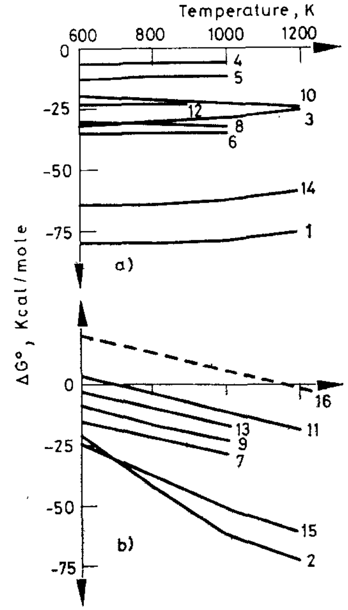

Fig. 4. Change in the isobaric-isothermal potential ΔG^0 of the reactions possible in the systems $CaO-V_2O_5$ (a) and $CaCO_3-V_2O_5$ (b) *vs.* temperature. The numbers of the curves here and in Figures 5 and 6 correspond to the numbers of equations

the sequence of the formation of new crystalline structures in the presence of the other components in excess, indicate the difficulty of interpreting these phenomena and the multiplicity of causes affecting them. In addition, some authors have been considering physicochemical transformations occuring in the course of gradual heating of the starting mixture of the components, while others reckoned with those taking place in the course of cooling the homogeneous melt of these components.

The thermodynamic analysis of the succession of chemical transformations is based on the thesis that the thermodynamic probability of the formation of compounds is a function of the change in the isobaric-isothermal potential of formation ΔG° of these compounds. We carried out the thermodynamic evaluation of the succession of transformations in the systems CaO $(CaCO_3)-V_2O_5$ by several methods. Their results and discussion follows.

(i) We compared the values of the changes in the isobaric-isothermic potential for all final and intermediate reactions possible in the given system. The reactions considered are listed in the followings. For simplicity, not the chemical formulae of the compounds, but the following symbols are used in the equations: $Ca = \mathrm{CaO}$; $V = \mathrm{V_2O_5}$; $C = \mathrm{CO_2}$; $Ca\mathrm{C} = \mathrm{CaCO_3}$.

1. $3\,Ca + V = Ca_3V$
2. $3\,CaC + V = Ca_3V + 3\,C$
3. $2\,Ca_3V + V = 3\,Ca_2V$
4. $Ca_2V + V = 2\,CaV$
5. $0.5\,Ca_3V + V = 1.5\,CaV$
6. $Ca + V = CaV$
7. $CaC + V = CaV + C$
8. $CaV + Ca = Ca_2V$
9. $CaV + CaC = Ca_2V + C$
10. $Ca_2V + Ca = Ca_3V$
11. $Ca_2V + CaC = Ca_3V + C$
12. $0.5\,CaV + Ca = 0.5\,Ca_3V$
13. $0.5\,CaV + CaC = 0.5\,Ca_3V + C$
14. $2\,Ca + V = Ca_2V$
15. $2CaC + V = Ca_2V + 2C$
16. $CaV = Ca + V$

The recalculation from 298° to the peritectic melting temperature of the corresponding calcium vanadates was carried out by the formula

$$\Delta G^\circ_T = \Delta H^\circ_{298} - T\Delta S^\circ_{298} + \Sigma\,[n_i(H^\circ_T - H^\circ_{298})_i] - T\,\Sigma\,[n_i(S^\circ_T - S^\circ_{298})_i]$$

using thermodynamic data from the literature [13]. The results (Fig. 4) indicate that all considered reactions proceed favourably from the thermodynamic view over practically the total temperature range studied. The minimum value of ΔG°_T corresponds to the reactions 1 and 2, i.e. to the formation of calcium orthovanadate from the starting components.

(ii) We compared the values of ΔG° of formation of the final compounds, calculated for the reactions, for whose left-hand sides the ratios of components are taken corresponding to all compounds of the system in question. By this method suggested in [11] we evaluated reactions 1, 14 and 6 in the system $CaO-V_2O_5$ and reactions 2, 15 and 7 in the system $CaCO_3-V_2O_5$. For both groups of reactions three variations of the calculation were carried out according to the calcium vanadates $Ca(VO_3)_2$, $Ca_2V_2O_7$ and $Ca_3(VO_4)_2$: the first, for the ratio of components being 1 : 1, the second for the ratio 2 : 1 and the third for the ratio 3 : 1.

The results of the analysis (Fig. 5) indicate that the minimum value of ΔG° corresponds to the formation reaction of differing vanadates in each of the variations, and the sequence of the decrease of ΔG° values for the different reactions is also not identical.

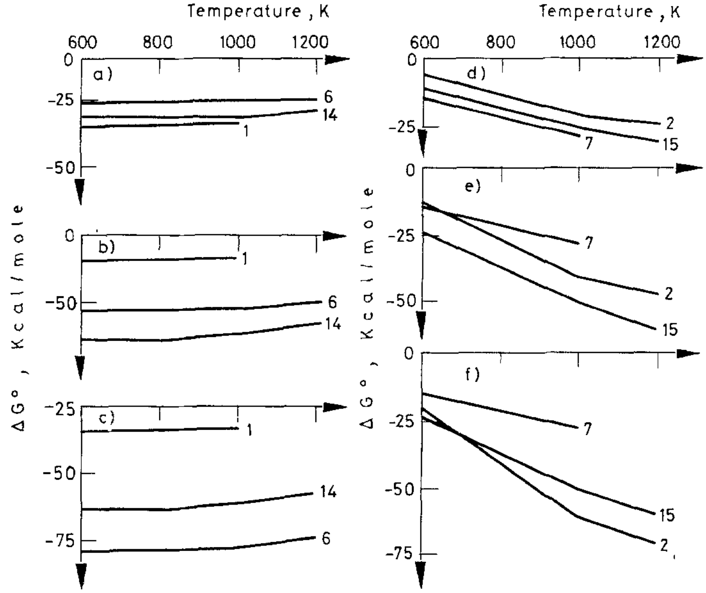

Fig. 5. Change in ΔG° *vs.* temperature for the compositions $CaO-V_2O_5$ 1 : 1 (a), 2 : 1 (b) and 3 : 1 (c), and $CaCO_3-V_2O_5$ 1 : 1 (d), 2 : 1 (e) and 3 : 1 (f)

(iii) We compared the probabilities of formation $P_{j,T}$ of the compounds in their capacity of primary compound, using the method described in [14]. The value $P_{j,T}$ for the compound $nM_pO_q \cdot mR_kO_l$ is calculated by means of the equation

$$P_{j,T} = -\frac{\Delta G^{\circ}_{j,T}}{n\Delta G^{\circ}_{a,Me_pO_q} + m\Delta G^{\circ}_{a,R_kO_l}}$$

where $\Delta G^{\circ}_{j,T}$ is the change in the isobaric-isothermal potential of formation of the binary-system compound from oxides, $\Delta G^{\circ}_{a,M_pO_q}$ and $\Delta G^{\circ}_{a,R_kO_l}$ are the changes in free energy at their dissociation into atoms.

An analogous calculation can also be performed if one of the starting substances is a carbonate. The maximum value of $P_{j,T}$, according to the opinion of the authors of the method, should correspond to the most probable primary product. Our calculations indicated (Fig. 6) that the thermodynamic probability of the formation, as primary product, in the systems CaO $(CaCO_3)-V_2O_5$ increases in the following sequence: $Ca(VO_3)_2-Ca_2V_2O_7-Ca_3(VO_4)_2$.

Turning now to the comparison of the experimental thermoanalytical results and the results of thermodynamic calculations, the contradiction is obvious.

Experimental data indicate a macrosuccession in which calcium content increases in each successively formed calcium vanadate. On the other hand, thermodynamic calculations, although contradictory in themselves (due perhaps to the imperfect approach and assumptions on which the suggested methods are based), tend to favour a succession of transformations from the orthovanadate to the pyrovanadate and subsequently to the metavanadate. This contradiction is presumably due to the fact that the succession of the reactions taking place in the studied systems cannot a priori be established on the basis of thermodynamic notions only. The controlling factor in this case is the kinetic aspect.

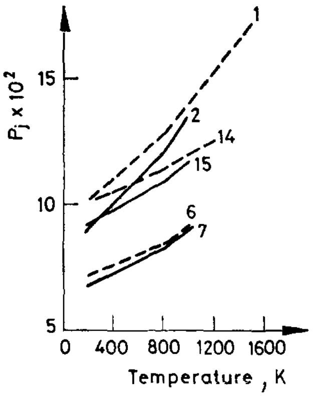

Fig. 6. Effect of temperature on the probability of formation P_j of calcium vanadates in the systems CaO (CaCO$_3$) — V$_2$O$_5$

Among all possible combinations of ΔG° values and the corresponding rates of reaction listed in [11], in the given case the combination in which the rate of reaction increases with decreasing ΔG° appears the most probable. In such cases, the primary compound formed is the one with minimum thermodynamic stability and the highest rate of reaction, that is, in our system, calcium metavanadate, and the final product the one with the minimum value of ΔG° and the minimum rate of reaction, that is, calcium orthovanadate. An unequivocal evidence for the succession of the chemical transformations in the CaO (CaCO$_3$)$-$V$_2$O$_5$ systems requires the knowledge of the kinetic relationships of these transformations, and also direct data on the mass transfer of the particles participating in the composition of the systems.

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Résumé — L'interaction de V_2O_5 avec l'oxyde de calcium et le carbonate de calcium a été étudiée par analyse thermique différentielle. Les résultats on indiqué que la succession des transformations de phase dans les systèmes $CaO-V_2O_5$ et $CaCO_3-V_2O_5$ correspond globalement à un accroissement de la teneur en calcium dans chaque vanadate de calcium successivement formé. Des calculs thermodynamiques effectués à l'aide des méthodes décrites dans la littérature pour déterminer les produits primaires et la succession des produits formés par la suite, montrent que les réactions chimiques qui ont lieu dans ces systèmes sont contrôlées par des facteurs cinétiques et non par des facteurs thermodynamiques.

Zusammenfassung — Die Wechselwirkungen von V_2O_5 mit Calciumoxid und Calciumcarbonat wurden durch Thermoanalyse untersucht. Die Ergebnisse zeigten, daß die Makro-Folge der Phasenänderungen in den Systemen $CaO-V_2O_5$ und $CaCO_3-V_2O_5$ bei jedem aufeinanderfolgenden Calciumvanadat einem zunehmenden Calciumgehalt entspricht. Die auf der Grundlage von in der Literatur empfohlenen Methoden durchgeführten thermodynamischen Berechnungen zur Bestimmung der Primärprodukte und der Reihenfolge der Sekundärprodukte ergaben, daß die in obigen Systemen vor sich gehenden Reaktionen durch kinetische und nicht durch thermodynamische Faktoren bedingt sind.

Резюме — Выполнено термоаналитическое исследование взаимодействия V_2O_5 с оксидом и карбонатом кальция. Показано, что при неизотермическом нагревании смеси макропоследовательность фазовых превращений в системах $CaO-V_2O_5$ и $CaCO_3-V_2O_5$ соответствует увеличению содержания кальция в каждом последующем образующемся ванадате кальция. Термодинамическая оценка по имеющимся в литературе способам определения первичного соединения и последовательного появления новых продуктов взаимодействия свидетельствует о том, что в рассматриваемых системах протекание химических реакций регулируется не термодинамическими, а кинетическими факторами.