Investigation of the kinetics of the reactions between sodium carbonate and oxides of transition metals[1]

N. Colović, M. Antonijević and S. Milić*

Technical Faculty Bor, University of Belgrade, 19 210 Bor (Minor Yugoslavia)

(Received 4 May 1992)

Abstract

The reactions between solid sodium carbonate and oxides of transition metals were investigated. The reactions were carried out under non-isothermal conditions and the degree of reaction was followed thermogravimetrically. Subsequent recording of TG curves showed that the reactions of Na_2CO_3 with oxides of iron, tungsten and vanadium proceed in one stage. Cr_2O_3 was found to react with sodium carbonate directly at lower temperatures, whereas at higher temperatures the dissociation of sodium carbonate also occurred. The reactions between sodium carbonate and oxides of titanium, manganese and molybdenum are complex and involve several stages. For all stages the activation energy and pre-exponential factor were determined and, by analyzing the values obtained, a kinetic compensation effect for three homologous reaction series was observed.

INTRODUCTION

The reactions between oxides of transition metals and other metal carbonates or oxides are of great interest because they give rise to reaction products having useful properties [1].

Iron oxide Fe_2O_3 is reactive at elevated temperatures, and its reactions with ZnO [2], NiO [3], MgO [4], Li_2CO_3 [5] and so on have been investigated. In powdered mixtures, Li_2CO_3 and Fe_2O_3 react at temperatures lower than the dissociation temperature of Li_2CO_3. The kinetics of this reaction are diffusion controlled and the activation energy is $210 \, kJ \, mol^{-1}$ over the range 653–783 K. The limiting stage is the diffusion of Li through the product layer of $LiFeO_2$ [5].

In the reactions of Cr_2O_3 with other metal oxides (CdO, CuO, MgO, NiO, ZnO), an intermediate chromate, which decomposes to MCr_2O_4, is formed. The diffusion of Cr^{3+} through the product layer and the transport of oxygen are the limiting stages [6].

Titanium(IV) oxide reacts with metal oxides or carbonates at elevated

---

temperatures to form the corresponding titanates. The reaction with barium carbonate was found to proceed with the formation of $BaTiO_3$ in the presence of carbon dioxide but, on removal of CO_2 from the system, Ba_2TiO_4 was formed [7, 8].

The reactions between metal carbonates and MO_3 $(M = Mo, W)$ are rather complex. The reactions of these oxides with other metal oxides are also interesting from both theoretical and practical aspects. The reaction of cobalt oxide with molybdenum(VI) oxide gives rise to a product which is used as an active and selective catalyst in organic syntheses [9]. The kinetics of this reaction are described by Jander's equation or the parabolic law. Its activation energy is $220\,kJ\,mol^{-1}$ over the range 793–923 K. The reaction with $CaCO_3$ was also investigated and was found to be diffusion controlled [10].

Manganese(IV) oxide decomposes at elevated temperatures, giving rise to a series of oxides [11]; the reaction is chemically controlled.

In investigations of the kinetics of catalytic reactions, a kinetic compensation effect [12, 13] was observed. The phenomenon of the kinetic compensation effect was also observed in other heterogeneous reactions [14–20], and recently also in reactions taking place under non-isothermal conditions [21–26]. In their papers many authors give interpretations of compensation parameters, but no satisfactory explanations or answers have so far been offered [27–35].

The present paper concerns the results obtained in investigations of the kinetics of reactions taking place between sodium carbonate and transition metal oxides (Fe_2O_3, Cr_2O_3, MnO_2, TiO_2, MoO_3, WO_3 and V_2O_5).

EXPERIMENTAL

All reagents used were of analytical grade.

Weight changes in the course of the reactions were followed on a Netzsch model 409 thermobalance, and the products obtained were subjected to X-ray analysis.

All experiments were performed using the same techniques. Firstly, an equimolar mixture of the reacting components (sodium carbonate + oxide) was homogenized, and then a definite amount (0.750 g) of the mixture was weighed and heated. Each reaction was investigated at different heating rates (2, 5, 10 and 20 K min^{-1}).

The kinetic curves $\alpha = f(T)$ or $\alpha = f(t)$ obtained at different linear heating rates were graphically differentiated, giving kinetic curves, which show the dependence of the reaction on the temperature or time ($d\alpha/dT$ or $d\alpha/dt$). From these curves were read the values for maximum reaction rates (V_{max}), and the corresponding temperatures (T_m) and treatment times (t_m).

RESULTS AND DISCUSSION

The kinetic curves obtained for the reactions between sodium carbonate and oxides of transition metals were analysed using the equations [36]

$$\frac{d \ln V_{max}}{d(1/T_m)} = -\frac{E}{R} \tag{1}$$

and

$$\frac{d \ln t_m}{d(1/T_m)} = \frac{E}{R} \tag{2}$$

where V_{max} is the maximum rate of the chemical reaction, determined from the first derivative of the curve $\alpha = f(T)$ or $\alpha = f(t)$; T_m is the temperature which corresponds to the maximum rate, and t_m denotes the time of treatment needed to attain the maximum rate. By the equation of Ozawa [37, 38]

$$\frac{d \ln q}{d(1/T_m)} = -\frac{E}{R} \tag{3}$$

where q denotes the linear heating rate.

The reactions between sodium carbonate and Fe_2O_3, WO_3 and V_2O_5, respectively, are less complex than the other reactions analysed, as they take place in one stage. These reactions can be represented as

$$Na_2CO_3 + Fe_2O_3 = 2NaFeO_2 + CO_2 \tag{4}$$
$$Na_2CO_3 + WO_3 = Na_2WO_4 + CO_2 \tag{5}$$
$$Na_2CO_3 + V_2O_5 = 2NaVO_3 + CO_2 \tag{6}$$

The reaction products were identified by X-ray analysis; Fig. 1 shows the diffractogram of the reaction product of (4), from which it is seen that $NaFeO_2$ is formed.

The kinetic curves $\alpha = f(T)$ for all the three reactions are of a similar character, and reaction (4) was chosen for the presentation of results. The kinetic curves obtained for this reaction (Fig. 2) were graphically differentiated (Fig. 3) in order to determine the maximum rate (V_{max}) and the corresponding temperature (T_m) and time (t_m). From these data, by using eqns. (1) and (2), which can be written in the developed form

$$\ln V_{max} = \ln A - \frac{E}{RT} \tag{7}$$

$$\ln t_m = \ln A + \frac{E}{RT} \tag{8}$$

the activation energy and the pre-exponential factor (A) were determined (Table 1). The activation energy was determined also by using eqn. (3), and no great deviations from the value calculated from eqns. (7) and (8) were found.
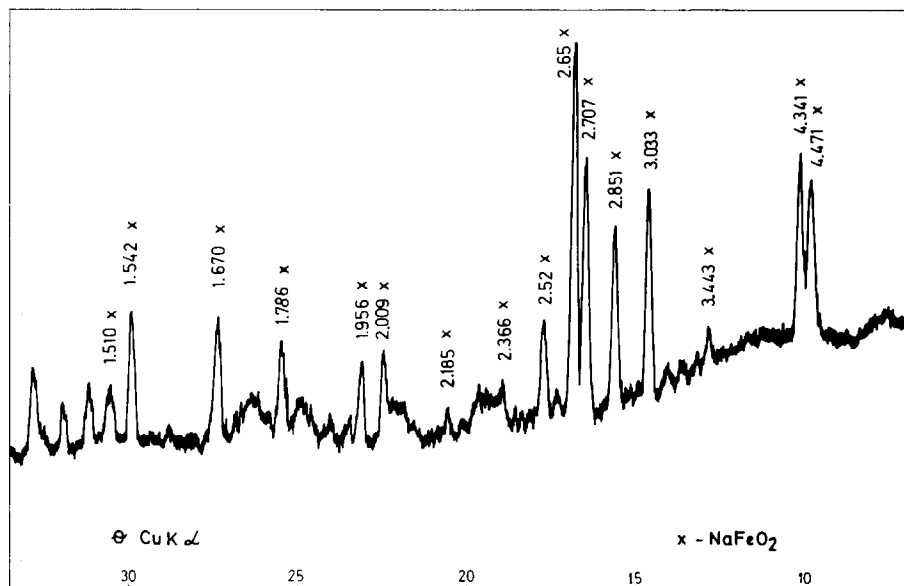
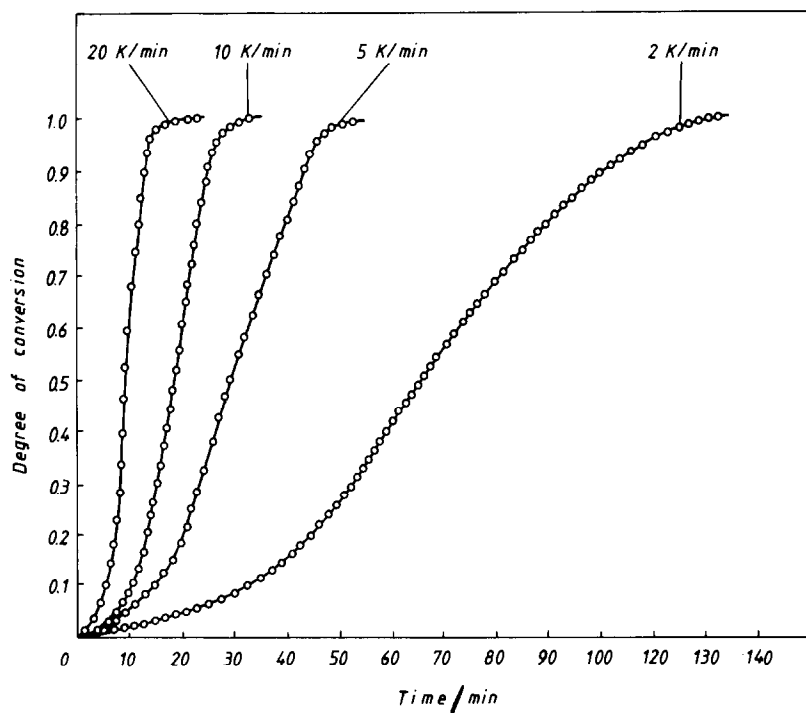Fig. 1. X-ray analysis of product of (4).

Fig. 2. Kinetic curves obtained for the reaction between Na_2CO_3 and Fe_2O_3 at different linear heating rates.
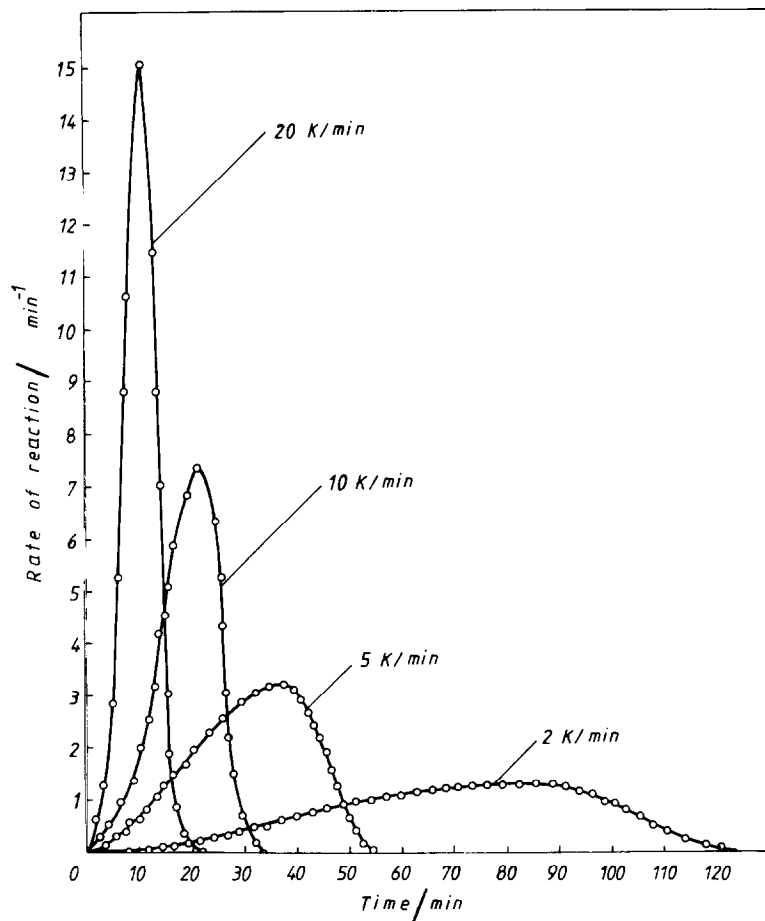
Fig. 3. Differential kinetic curves obtained for the reaction between Na_2CO_3 and Fe_2O_3 at different linear heating rates.

Similarly, it was found that the temperatures corresponding to the maximum rate of the chemical reaction were lower than the dissociation temperature of sodium carbonate (1125 K), indicating that reactions (4), (5) and (6) are correct.

From Fig. 5 which shows the differential kinetic curves obtained for the reaction between sodium carbonate and Cr_2O_3, it is seen that this reaction proceeds in two stages. The first peak on the differential curve corresponds most probably to the reaction

$$Na_2CO_3 + Cr_2O_3 = 2NaCrO_2 + CO_2 \qquad (9)$$
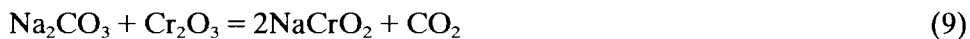
This reaction represents the first stage. The temperatures corresponding to the maximum rate of the chemical reaction in the first stage are lower than the dissociation temperature of Na_2CO_3, and are in the range 733–823 K, depending on the heating rate. These findings show that in this

TABLE 1

Kinetic parameters in the reactions between sodium carbonate and oxides of transition metals

No.	Reactions of Na_2CO_3 with oxides of transition metals	Eqn. (1)		Eqn. (2)		Eqn. (3)
		$E/$ $(kJ\,mol^{-1})$	$A/$ (min^{-1})	$E/$ $(kJ\,mol^{-1})$	$A/$ (min^{-1})	$E/$ $(kJ\,mol^{-1})$
	$Na_2CO_3 + TiO_2$					
1	Stage I	199	5.1×10^{11}	252	1.2×10^{12}	246
2	Stage II	194	1.3×10^{10}	232	7.2×10^{8}	223
3	Stage III	534	5.8×10^{23}	726	5.1×10^{28}	664
	$Na_2CO_3 + V_2O_5$					
4	Direct	636	3.9×10^{40}	790	4.1×10^{48}	737
	$Na_2CO_3 + Cr_2O_3$					
5	Stage I	71	3.5×10^{5}	93	2.2×10^{4}	111
6	Stage II	68	8.3×10^{3}	65	4.0×10^{1}	78
	$Na_2CO_3 + MoO_3$					
7	Stage I	250	4.0×10^{19}	316	4.5×10^{21}	315
8	Stage II	296	3.5×10^{20}	374	4.3×10^{22}	368
9	Stage III	508	4.9×10^{28}	623	1.2×10^{37}	587
10	Stage IV	400	6.0×10^{24}	584	7.8×10^{33}	568
	$Na_2CO_3 + WO_3$					
11	Direct	333	1.4×10^{21}	546	2.0×10^{30}	520
	$Na_2CO_3 + MnO_2$					
12	Stage I	191	3.3×10^{11}	262	4.8×10^{13}	215
13	Stage II	160	1.7×10^{7}	162	1.7×10^{4}	172
14	Stage III	130	6.5×10^{4}	125	9.4×10^{2}	136
	$Na_2CO_3 + Fe_2O_3$					
15	Direct	300	3.7×10^{14}	249	2.2×10^{10}	278

system reaction (9) occurs. From the kinetic curves it can be observed that, at higher temperatures (longer time of treatment), within the temperature range corresponding to the first stage, another stage also takes place. This second stage points to a change of the reaction mechanism, and can be explained by assuming that at higher temperatures the reaction most probably proceeds in the following manner: (a) decomposition of sodium carbonate

$$Na_2CO_3 = Na_2O + CO_2 \tag{10}$$

(b) reaction between Na_2O and chromium oxide

$$Na_2O + Cr_2O_3 = 2NaCrO_2 \tag{11}$$

The reaction product (Fig. 6) indicates that in the course of treatment the following reaction (c) may also take place

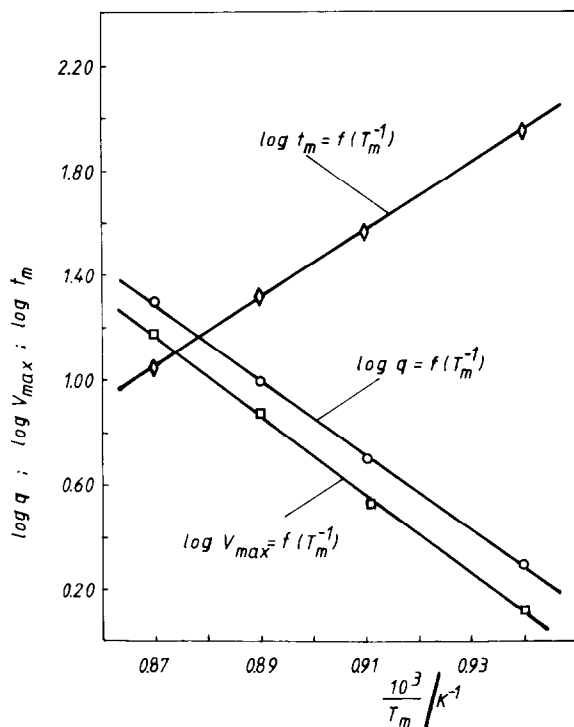$$Na_2CO_3 + 0.5Cr_2O_3 + 0.75O_2 = Na_2CrO_4 + CO_2 \tag{12}$$

Fig. 4. Plots of $\log q$, $\log V_{max}$ and $\log t_m$ versus T_m^{-1}.

In reaction (a) a loss of mass occurs, whereas in reaction (c) the mass is increased; the total effect was found to be a decrease of mass.

The temperature T_m which corresponds to stage II increases with increasing heating rate, and at a heating rate of $20\ K\ min^{-1}$ T_m is 1233 K. This fact supports the mechanism proposed.

The activation energy and the pre-exponential factor were determined for both stage I and stage II (Table 1).

The kinetic curves (in the differential form) obtained in investigating the reactions between Na_2CO_3 and TiO_2, and between Na_2CO_3 and MnO_2, were more complex than those previously analysed, as these curves showed peaks (Fig. 7) indicating that, with increasing temperature, three stages are observed.

The first stage (the first peak) relates to a direct reaction between Na_2CO_3 and TiO_2 (eqn. (13)) or MnO_2, since the temperatures corresponding to the maxima rates are lower than the dissociation temperature of sodium carbonate (T_m for reaction (13) is in the range 843–913 K). The temperature range for the reaction between Na_2CO_3 and MnO_2 is 888–953 K.

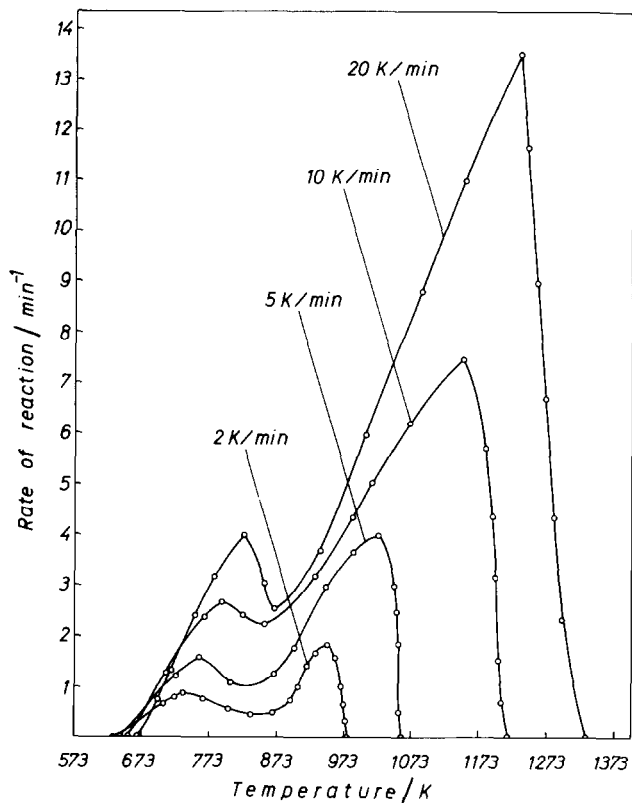$$Na_2CO_3 + TiO_2 = Na_2TiO_3 + CO_2 \tag{13}$$

Fig. 5. Differential kinetic curves obtained for the reaction between Na_2CO_3 and Cr_2O_3 at different linear heating rates.
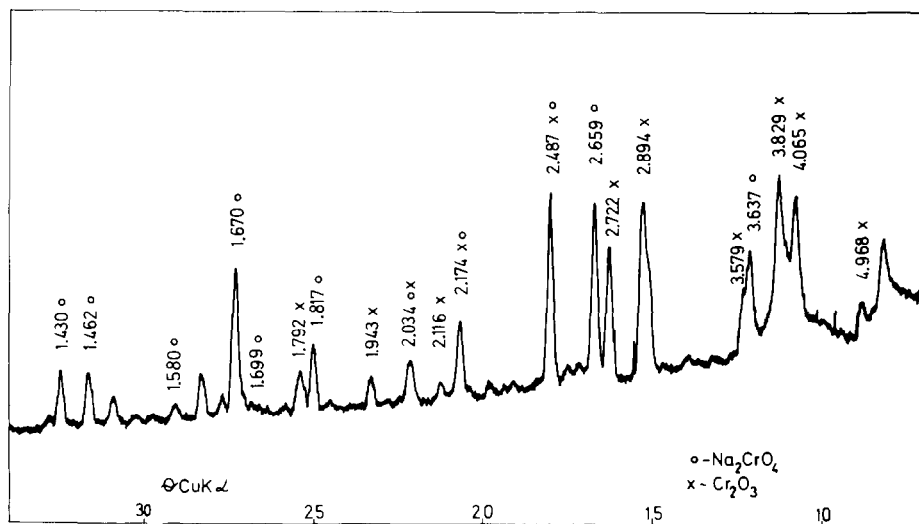

Fig. 6. X-ray analysis of the reaction product in the reaction between Na_2CO_3 and Cr_2O_3.
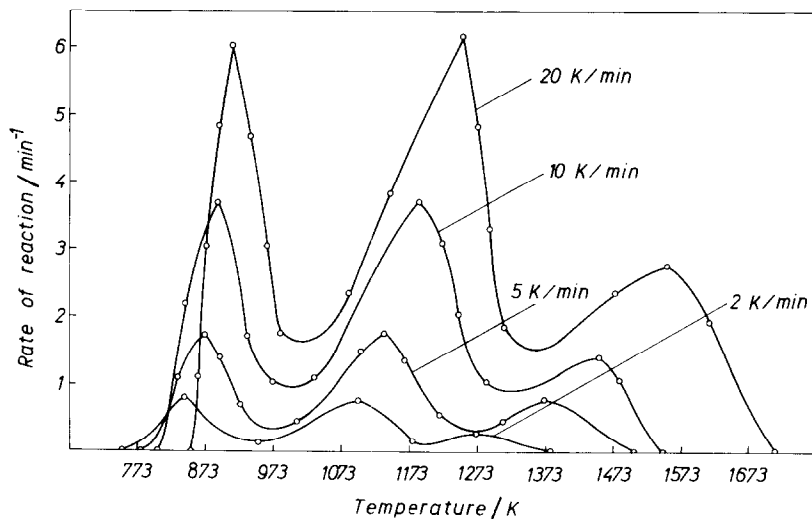
Fig. 7. Differential kinetic curves obtained for the reaction between Na_2CO_3 and MnO_2 at different linear heating rates.

The second stage (stage II) can be interpreted in the same manner as in the reaction of Na_2CO_3 with Cr_2O_3

(a) $Na_2CO_3 = Na_2O + CO_2$ (10)

(b) $Na_2O + TiO_2 = Na_2TiO_3$ (14)

The temperatures corresponding to V_{max} are higher than 1125 K, corresponding to the mechanism proposed.

The third stage most probably corresponds to the formation of polynuclear complexes of titanium or manganese with elimination of oxygen (Fig. 7).

The reaction between Na_2CO_3 and MoO_3 is the most complex of all the reactions investigated, as may be seen from kinetic curves shown in Fig. 8.

The kinetic curves obtained indicate that in this reaction, with increasing temperature, there appear four stages.

The first stage represents the direct synthesis between Na_2CO_3 and MoO_3 and proceeds at the lowest temperatures ($T_m = 683$–715 K)

$$Na_2CO_3 + MoO_3 = Na_2MoO_4 + CO_2$$ (15)

The second and third stages most probably represent the formation of polynuclear complexes of molybdenum, since molybdenum is easily polymerized with liberation of oxygen. These stages are at a far lower temperature (789–853 K) than that of sodium carbonate dissociation.

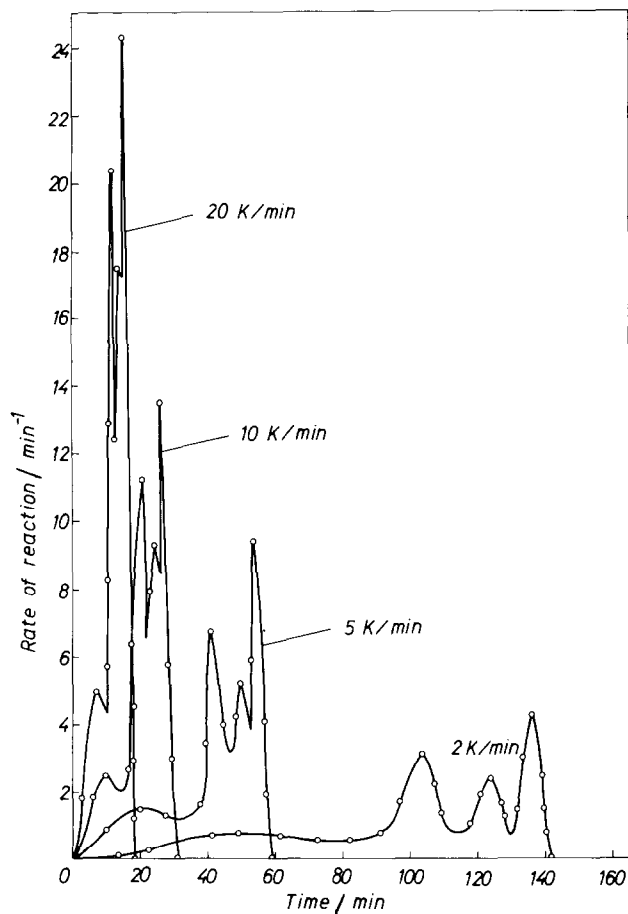The fourth stage most probably involves the sublimation of MoO_3.

Fig. 8. Differential kinetic curves obtained for the reaction of Na_2CO_3 with MoO_3 at different linear heating rates.

The activation energy and the pre-exponential factor were determined as already shown (Table 1). The values for the activation energy and the pre-exponential factor are high, whereas the kinetic curves obtained are of a sigmoidal form, indicating that the investigated reactions are chemically controlled [36, 39, 40].

Considering the values for the activation energy and the pre-exponential factors (Table 1), as well as the graphical presentation of the dependence $\ln A = f(E)$, it may be observed that, in the system of reactions between Na_2CO_3 and transition metal oxides, there is a kinetic compensation effect (Fig. 9), which can be written in the form of the equation

$$\ln A = a + bE \tag{16}$$
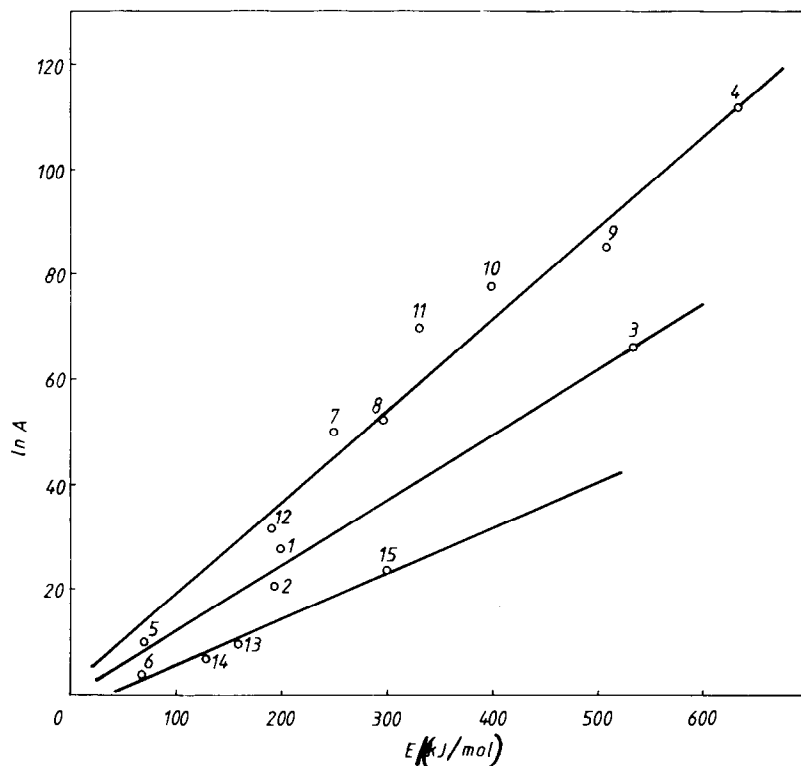
where a and b are the compensation constants.

Fig. 9. Compensation effect.

Three homologous series of reactions were found, in which the compensation constants for the first series are $a = 1.66$, $b = 0.177$; for the second series: $a = -0.42$, $b = 0.125$; and for the third series: $a = -3.73$, $b = 0.090$. The compensation constants were obtained by regression analysis, the correlation coefficients being 0.985, 0.990 and 0.991 for the first, the second and the third series, respectively.

On the diagram in Fig. 9, the points designated by numbers from 1 to 15 denote the corresponding reactions and stages given in Table 1.

The experimentally obtained order of decreasing reactivity in the reactions between sodium carbonate and oxides of transition metals in the first series is given in Table 2. It can be noticed that the reactivity

TABLE 2

Order of reactivity

$Na_2CO_3 + Cr_2O_3$	Stage I	$Na_2CO_3 + WO_3$	Direct
$Na_2CO_3 + MnO_2$	Stage I	$Na_2CO_3 + MoO_3$	Stage IV
$Na_2CO_3 + MoO_3$	Stage I	$Na_2CO_3 + MoO_3$	Stage III
$Na_2CO_3 + MoO_3$	Stage II	$Na_2CO_3 + V_2O_5$	Direct

decreases with increasing atomic number in the corresponding group of the Periodic Table of the elements (chromium oxide reacts more strongly with sodium carbonate than tungsten oxide: Periodic Group VIA).

CONCLUSIONS

(1) The reactions between Na_2CO_3 and WO_3, and between Fe_2O_3 and V_2O_5, are one-stage reactions. The most intense reaction is the formation of $NaFeO_2$.

(2) The reaction between Na_2CO_3 and Cr_2O_3 is a two-stage reaction.

(3) TiO_2 and MnO_2 react with Na_2CO_3 in such a manner that, with increasing temperature, the reaction mechanism is changed and the reactions proceed in three stages.

(4) The reaction between Na_2CO_3 and MoO_3 involves four stages.

(5) The kinetic compensation effect indicates that, in the system of reactions between Na_2CO_3 and transition metal oxides, there are three homologous series of reactions.

REFERENCES

1 P.P. Budnikov and A.M. Ginstling, Reakcii v smesyah tverdyh veshchestv, Stroizdat, Moscow, 1971.
2 G. Huttig, Z. Electrochem., 41 (1935) 429.
3 R. Parker, C.J. Rigden and C.J. Tinsley, Trans. Faraday Soc., 65 (1969) 219.
4 S.F. Hulbert, H.H. Wilson and D.A. Venkatu, Trans. Br. Ceram. Soc., 69 (1970) 9.
5 P.K. Gallagher and D.W. Johnson, J. Am. Ceram. Soc., 59 (1976) 171.
6 H. Charcosset, P. Turlier and Y. Trambouze, J. Chim. Phys., 47 (1964) 1249.
7 R.M. Dell, Inst. Chem. Eng. Symp. Ser., 27 (1968) 3.
8 T. Yamaguchi, S.H. Cho, H. Nagai and H. Kuno, Reactivity of Solids, Proc. 8th Int. Symp., Plenum Press, New York, 1977, 701.
9 T. Bak, J. Haber and J. Ziolkowski, J. Solid State, 16 (1976) 83.
10 C. Das, Thermochim. Acta, 144 (1989) 363.
11 M.A. Reuter and J.S.J. Deventer, Thermochim. Acta, 125 (1989) 99.
12 J.M. Thomas and W.J. Thomas, Introduction to the Principles of Heterogeneous Catalysis, Academic Press, New York, 1967, 263.
13 J. Zsako, J. Therm. Anal., 9 (1976) 101.
14 P.D. Garn, J. Therm. Anal., 7 (1975) 475.
15 P.D. Garn, J. Therm. Anal., 10 (1976) 99.
16 D. Dollimore and T.J. Taylor, Thermochim. Acta, 40 (1980) 302.
17 V.M. Gorbachev, J. Therm. Anal., 9 (1976) 21.
18 A.V. Nikolaev, V.A. Logvinenko and V.M. Gorbachev, J. Therm. Anal., 6 (1974) 473.
19 J. Zsako, J. Therm. Anal., 5 (1973) 239.
20 M.M. Pavlynchenko, E.A. Prodan and S.A. Slyshkina, Dokl. Akad. Nauk SSSR, 181 (1968) 1174.
21 S. Bordas, M.T. Clavaguera-Mora and N. Clavaguera, Thermochim. Acta, 133 (1988) 296.
22 P.V. Khadikar, Thermochim. Acta, 127 (1988) 37.
23 N. Koga and H. Tanaka, Thermochim. Acta, 135 (1988) 79.
24 J. Pysiak, Thermochim. Acta, 148 (1989) 169.

25 P. Bukovec and N. Bukovec, Thermochim. Acta, 149 (1989) 53.
26 T. Cordero, F. Garcia and J.J. Rodriguez, Thermochim. Acta, 149 (1989) 225.
27 J. Pysiak and B. Sabalski, J. Therm. Anal., 17 (1979) 287.
28 D.J. Brown, Thermochim. Acta, 54 (1982) 377.
29 L. Stoch, Thermochim. Acta, 148 (1989) 149.
30 J.P. Elder, J. Therm. Anal., 36 (1990) 1077.
31 K.N. Ninan, K.B. Catherine and K. Krishnan, J. Therm. Anal., 36 (1990) 855.
32 J.H. Flynn, J. Therm. Anal., 37 (1991) 347.
33 N. Koga and J. Šesták, J. Therm. Anal. 37 (1991) 1103.
34 T.C. Vaimakis, P.J. Pomonis and A.T. Sdoukos, Thermochim. Acta, 173 (1990) 101.
35 I.C. Hoare and J.H. Levy, Thermochim. Acta, 164 (1990) 153.
36 N. Colovich and M. Antich, Zh. Fiz. Khim., 58 (1984) 2710.
37 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
38 T. Ozawa, J. Therm. Anal., 2 (1970) 301.
39 B. Delmon, Kinetika geterogennych reakcii, Mir, Moscow, 1972.
40 A. Bartecki and L. Rycerz, Hydrometallurgy, 20 (1988) 235.