ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 3, pp. 409–414. © Pleiades Publishing, Ltd., 2013.
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Equilibrium Composition and Initial Rate of the Reversible Solid Phase Reaction in the System Na_2CO_3–$BaSO_4$–Na_2SO_4–$BaCO_3$

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Received January 17, 2012

Abstract—The results of experimental study of reversible solid-state reaction $Na_2CO_3 + BaSO_4 = Na_2SO_4 + BaCO_3$ were considered. The equilibrium composition of the mixture at 550 and 600°C with 10 different initial ratios of the reactants, and the initial rate of the process were determined. The role of the Le Chatelier principle in the analysis of the thermodynamic state of the reagents was considered. The thermodynamic equilibrium constant was found from the data on the dependence of concentration equilibrium constants on the composition and the results of X-ray phase analysis using regular solution theory.

DOI: 10.1134/S1070363213030018

Investigation of kinetics and thermodynamics of reversible solid-state reactions is a complicated experimental task for several reasons. Firstly, most of the solid-state reactions are irreversible and proceed till the exhaustion of one of the reactants. Secondly, due to steric hindrances, the time of reaching equilibration in these reactions is large enough. Thirdly, the study of the direct and reverse reaction are possible only when these reactions proceed at rates that allow accurate measurements. Fourthly, a method of separation and analysis of solid mixtures is required, which would allow a reliable determination of the content of the components in the reaction mixture. As showed the analysis of the literature, the allotropic transformation of solids are the most frequently studied. Actual reversible and solid-state reactions have been much less studied [1]. In this paper we studied the rate and equilibrium of a reversible solid-state reaction $Na_2CO_3 + BaSO_4 = Na_2SO_4 + BaCO_3$, the first indication of the reversibility of which was observed in [2].

The composition of the initial reaction mixture and the temperature of the experiments are presented in Table 1. Initially weighed samples of reagents were thoroughly ground in a porcelain mortar. To determine the equilibrium compositions the mixtures, approximately 200 mg, with the compositions corresponding to the initial composition of the forward and reverse reactions were placed in two quartz tubes, and both tubes were placed together in a tubular resistance furnace pre-heated to the temperature of the experiment. Samples were kept at the desired temperature for 2 h, then allowed to cool, carefully ground in a mortar and again heated in the oven. The procedure was repeated 4 times. It was found experimentally that this was sufficient to achieve the equilibrium sample composition: compositions were identical within the error of analysis in both tubes. For each initial composition the experiments were performed at least 3 times. Analysis of the mixtures is described in Experimental. The equilibrium compositions of the investigated compounds are shown in Table 2, and the data on the initial rates, in Table 3.

The degree of conversion (α) for all studied reactions was calculated by the formula (1):

$$\alpha = \Delta m/\Delta m_{\max}, \tag{1}$$

where Δm is a gain in weight of the product or a loss in weight of a reactant, $\Delta m_{\max}$ is the maximum possible loss in weight of a reactant or product in the case of irreversible reaction in the same direction.

The XRD phase analysis of the equilibrium mixtures showed that the qualitative composition of

Table 1. The initial composition of the reaction mixtures

Forward reaction	Molar ratio of the components	Reverse reaction	Molar ratio of the components
Na_2CO_3:$BaSO_4$	1:1	Na_2SO_4:$BaCO_3$	1:1
Na_2CO_3:$BaSO_4$	1:2	Na_2SO_4:$BaCO_3BaSO_4$	1:1:1
Na_2CO_3:$BaSO_4$	2:1	Na_2SO_4:$BaCO_3$:Na_2CO_3	1:1:1
Na_2CO_3:$BaSO_4$:Na_2SO_4	1:1:1	Na_2SO_4:$BaCO_3$	2:1
Na_2CO_3:$BaSO_4$:$BaCO_3$	1:1:1	Na_2SO_4:$BaCO_3$	1:2

Table 2. The equilibrium composition of the reaction mixtures

Initial molar composition	Equilibrium molar composition							
	550°C				600°C			
	Na_2CO_3	$BaSO_4$	Na_2SO_4	$BaCO_3$	Na_2CO_3	$BaSO_4$	Na_2SO_4	$BaCO_3$
Na_2CO_3:$BaSO_4$ = 1:1	0.21	0.21	0.29	0.29	0.18	0.18	0.32	0.32
Na_2SO_4:$BaCO_3$ = 1:1	0.20	0.20	0.30	0.30	0.19	0.19	0.31	0.31
Na_2CO_3:$BaSO_4$ = 1:2	0.18	0.52	0.15	0.15	0.13	0.47	0.20	0.20
Na_2SO_4:$BaCO_3$:$BaSO_4$ = 1:1:1	0.19	0.52	0.14	0.14	0.14	0.47	0.195	0.195
Na_2CO_3:$BaSO_4$ = 2:1	0.41	0.076	0.26	0.26	0.35	0.021	0.31	0.31
Na_2SO_4:$BaCO_3$:Na_2CO_3 = 1:1:1	0.40	0.069	0.26	0.26	0.36	0.023	0.31	0.31
Na_2CO_3:$BaSO_4$:Na_2SO_4 = 1:1:1	0.26	0.26	0.41	0.072	0.23	0.23	0.43	0.10
Na_2SO_4:$BaCO_3$ = 2:1	0.26	0.26	0.43	0.093	0.23	0.23	0.44	0.11
Na_2CO_3:$BaSO_4$:$BaCO_3$ = 1:1:1	0.19	0.19	0.15	0.48	0.15	0.15	0.19	0.53
Na_2SO_4:$BaCO_3$ = 1:2	0.19	0.19	0.15	0.48	0.15	0.15	0.19	0.52

Table 3. The conversion in the forward and reverse reactions with different initial compositions within 10 min

Forward reaction			Reverse reaction		
Initial composition	550°C	600°C	Initial composition	550°C	600°C
Na_2CO_3:$BaSO_4$ = 2:1	0.18	0.56	Na_2SO_4:$BaCO_3$ = 2:1	0.29	0.39
Na_2CO_3:$BaSO_4$ = 1:1	0.11	0.15	Na_2SO_4:$BaCO_3$ = 1:1	0.23	0.25
Na_2CO_3:$BaSO_4$ = 1:2	0.21	0.47	Na_2SO_4:$BaCO_3$ = 1:2	0.28	0.35
Na_2CO_3:$BaSO_4$:Na_2SO_4 = 1:1:1	0.05	0.06	Na_2SO_4:$BaCO_3$:$BaSO_4$ = 1:1:1	0.17	0.23
Na_2CO_3:$BaSO_4$:$BaCO_3$ = 1:1:1	0.07	0.12	Na_2SO_4:$BaCO_3$:Na_2CO_3 = 1:1:1	0.02	0.05

the equilibrium mixture in the forward and reverse reaction is the same, that is, the systems under study really reacted reversibly.

As can be seen from Table 2, the equilibrium composition in the system Na_2CO_3–$BaSO_4$–Na_2SO_4–$BaCO_3$ strongly depends on the initial composition of the mixture and slightly depends on temperature. When the temperature increases the concentration of the products of the direct reaction $Na_2CO_3 + BaSO_4 \rightarrow Na_2SO_4 + BaCO_3$ increases, that is, in the range of the studied temperatures the reverse reaction occurs with heat absorption. The calculation of the equilibrium constant of this reaction must take into account that when one or more solid compounds are involved in a solid phase reaction, their activity is identically equal to 1, and it can be omitted in the expression for the equilibrium constant [3]. Therefore, to calculate the equilibrium constant of the reaction under study it is absolutely necessary to know the phase composition of the mixture and the nature of the possible solid solutions. The XRD phase analysis of equilibrium mixtures showed that they contain only two substances, $BaSO_4$ and $BaCO_3$, as the pure solid phases. In all the samples studied the pure solid phases of Na_2CO_3 and Na_2SO_4 were not found. After accounting for the interplanar distances corresponding to pure phases, the remaining reflections, according to the ASTM database of interplanar distances, were identified as a phase of the Na_2CO_3–Na_2SO_4 solid solution of variable composition. Naturally, the activities of these particular substances determine the equilibrium composition of the mixture. For independent verification of this conclusion we analyzed the experimental data from the position of the Le Chatelier principle. If our understanding of the phase composition of the equilibrium mixture is correct, then adding sodium carbonate to the system should increase the yield in the forward reaction Na_2CO_3 + $BaSO_4$, while adding sodium sulfate should reduce it. Similarly, in the case of the reverse reaction Na_2SO_4 + $BaCO_3$, adding sodium sulfate to the system should increase the yield of the reaction, while adding sodium carbonate should reduce it. Addition of barium carbonate or sulfate should not significantly affect the equilibrium composition of the two reactions, because it cannot affect the composition of the equilibrium solid solution. Figure 1 shows conversion of sodium carbonate in the reaction for the initial mixtures of different composition. As can be seen, the addition to the system of sodium carbonate or sodium sulfate strongly influences the equilibrium conversion for any initial composition of the mixture. The change in the degree of conversion reaches 40–90% in accordance with the Le Chatelier principle. When $BaCO_3$ or $BaSO_4$ was added to the mixture, the reaction yield in most cases did not change significantly. Thus, in this system there are two pure solid phases in equilibrium, $BaCO_3$ and $BaSO_4$, and a solid solution Na_2CO_3–Na_2SO_4. Therefore, to calculate the concentration equilibrium constant K of the reaction Na_2CO_3 + $BaSO_4 \rightarrow Na_2SO_4 + BaCO_3$ formula (2) should be used

$$K_x = x(Na_2SO_4)/x(Na_2CO_3), \quad (2)$$

where x is the mole fraction of reactant or product in the solid solution [3]. The concentration equilibrium constants calculated by this formula are listed in Table 4. As can be seen, the concentration equilibrium constant for all the compounds is close to 1, it slightly increases with increasing temperature and is highly dependent on the initial composition of the reaction mixture. This is due to the fact that the solid solution is not ideal.

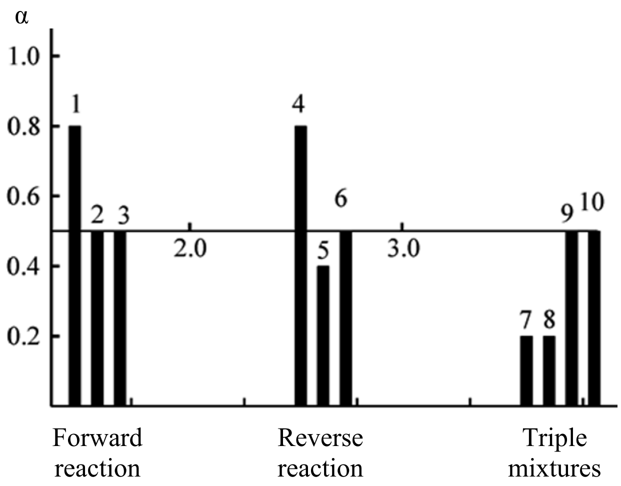

Fig. 1. Effect of reagent addition on the equilibrium degree of conversion. (1) [$2Na_2CO_3$ + $BaSO_4$], (2) [Na_2CO_3 + $BaSO_4$, (3) [Na_2CO_3 + $2BaSO_4$], (4) [$2Na_2SO_4$ + $BaCO_3$], (5) [Na_2SO_4 + $BaCO_3$], (6) [Na_2SO_4 + $2BaCO_3$], (7) [Na_2CO_3 + Na_2SO_4 + $BaCO_3$], (8) [Na_2SO_4 + Na_2CO_3 + $BaSO_4$], (9) [Na_2SO_4 + $BaCO_3$ + $BaSO_4$], (10) [Na_2CO_3 + $BaSO_4$ + $BaCO_3$].

To calculate the thermodynamic equilibrium constant of this reaction it is necessary to know the activity coefficients of Na_2CO_3 and Na_2SO_4 in the solid solution. For their calculation, we applied the model of regular solutions [4]. According to this model, the activity coefficients of the substance in a two-component solid solution in the absence of excess

Table 4. Concentration equilibrium constants K_x for the reaction Na_2CO_3 + $BaSO_4$ = Na_2SO_4 + $BaCO_3$ at two temperatures in the mixtures of different initial composition

Initial molar composition	550°C	600°C
$Na_2CO_3:BaSO_4$ = 1:1	1.4	1.8
$Na_2SO_4:BaCO_3$ = 1:1	1.5	1.6
$Na_2CO_3:BaSO_4$ = 1:2	0.83	1.5
$Na_2SO_4:BaCO_3:BaSO_4$ = 1:1:1	0.74	1.4
$Na_2CO_3:BaSO_4$ = 2:1	0.63	0.89
$Na_2SO_4:BaCO_3:Na_2CO_3$ = 1:1:1	0.65	0.86
$Na_2CO_3:BaSO_4:Na_2SO_4$ = 1:1:1	1.6	1.9
$Na_2SO_4:BaCO_3$ = 2:1	1.7	1.9
$Na_2CO_3:BaSO_4:BaCO_3$ = 1:1:1	0.79	1.4
$Na_2SO_4:BaCO_3$ = 1:2	0.79	1.3

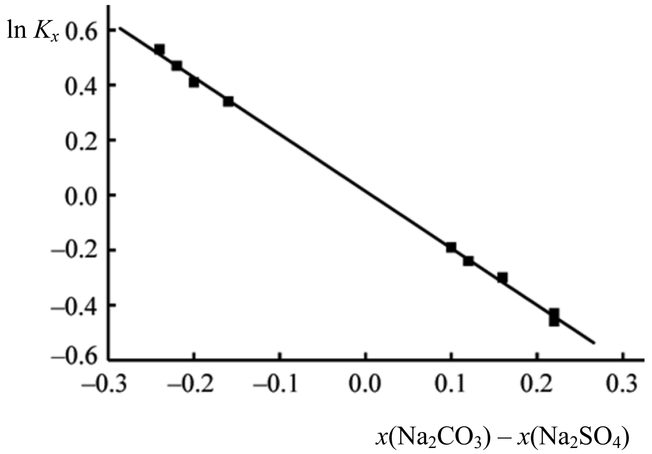

Fig. 2. Dependence of the thermodynamic equilibrium constant ln K_x–$F[x(Na_2CO_3) - x(Na_2SO_4)]$ in the coordinates at 550°C.

mixing volume can be calculated using the following formulas (3) and (4),

$$RT\ln \gamma_1 = \alpha x_2^2, \qquad (3)$$

$$RT\ln \gamma_2 = \alpha x_1^2, \qquad (4)$$

where x_1, x_2 are the mole fractions of the mixture components, γ_1, γ_2 are their activity coefficients, α is the energy parameter, which reflects the interaction energy of the species 1 and 2 with each other, T is the temperature of the mixture.

The thermodynamic equilibrium constant (K_a) in the reaction $Na_2CO_3 + BaSO_4 = Na_2SO_4 + BaCO_3$ can be calculated by the formula (5):

$$\begin{aligned} K_a &= a(Na_2SO_4)/a(Na_2CO_3) \\ &= [\gamma(Na_2SO_4)/\gamma(Na_2CO_3)]\cdot[x(Na_2SO_4)/x(Na_2CO_3)] \\ &= [\gamma(Na_2SO_4)/\gamma(Na_2CO_3)]K_x. \qquad (5) \end{aligned}$$

From (5) we obtain:

$$\ln K_a = \ln [\gamma(Na_2SO_4)/\gamma(Na_2CO_3)] + \ln K_x. \qquad (6)$$

From Eq. (3) and (4) we obtain an expression for calculating the logarithm of the activity coefficients of sodium carbonate and sodium sulfate in the solid solution:

$$\begin{aligned} &\ln [\gamma(Na_2SO_4)/\gamma(Na_2CO_3)] \\ &= (\alpha/RT)[x^2(Na_2CO_3) - x^2(Na_2SO_4)] \\ &= (\alpha/RT)[x(Na_2CO_3) - x(Na_2SO_4)]. \qquad (7) \end{aligned}$$

T, °C	α/RT	ln K_a	Correlation coefficient
550	2.1	0.014	0.999
600	2.0	0.011	0.990

Here we used the identity $x(Na_2CO_3) + x(Na_2SO_4) = 1$, and the relations: $x^2(Na_2CO_3) - x^2(Na_2SO_4) = [x(Na_2CO_3) - x(Na_2SO_4)]\cdot[x(Na_2CO_3) + x(Na_2SO_4)] = x(Na_2CO_3) - x(Na_2SO_4)$.

From Eq. (6) and (7) we get Eq. (8):

$$\ln K_x = \ln K_a - (\alpha/RT)[x(Na_2CO_3) - x(Na_2SO_4)]. \qquad (8)$$

Thus, the experimental data on the equilibrium composition must lie on a straight line in the coordinates ln K_x – $x(Na_2CO_3) - x(Na_2SO_4)$ with the slope $-(\alpha/RT)$ and the constant term –ln K_a. The experimental data at 550°C in these coordinates are shown in Fig. 2. Table 5 shows the results of the calculation of the parameters of Eq. (8) by the least squares method. As seen from Fig. 2 and the tables, the experimental data at two temperatures really well obey the linear correlation in the specified coordinates. The thermodynamic equilibrium constant for the reaction under study is weakly temperature dependent and is approximately equal to 1. The calculation of α showed that at both temperatures, $\alpha \approx 14.5$ kJ mol^{-1}. Indeed, in the investigated temperature range the α value should remain constant, as at a change in temperature of 50°C the interionic interactions in the solid solution remain virtually unchanged.

The experimental values of the thermodynamic equilibrium constants for the studied reaction should be compared with the equilibrium constants that can be calculated from the reference thermodynamic data. This calculation was made on the thermodynamic data from [5]. The thermodynamic characteristics of the reaction at two temperatures were found to be as follows: $\Delta H^0(550°C) = 3.54$ kJ mol^{-1}, $\Delta S^0(550°C) = 13.4$ J mol^{-1} K^{-1}, $\Delta G^0(550°C) = -7.51$ kJ mol^{-1}, $\Delta H^0(600°C) = 3.35$ kJ mol^{-1}, $\Delta S^0(600°C) = 13.2$ J mol^{-1} K^{-1}, $\Delta G^0(600°C) = -8.16$ kJ mol^{-1}. As can be seen, all the quantities are very small and close to zero. Thus, the thermodynamic equilibrium constant of the reaction studied should be close to 1 and weakly dependent on temperature. This conclusion is fully supported by our experimental data.

Figure 3 shows the degree of conversion of the initial composition of the mixture in the reaction $Na_2CO_3 + BaSO_4$ at two temperatures in the initial 10 min. The minimum degree of transformation occurs at the stoichiometric composition (1:1). The quantitative description of these dependences is given in [6, 7]. Since the solid-state reaction takes place in the contact points between the reactants, the relative increase in the content of a component increases the number of contacts between them, which leads to increased rate of solid-state reaction. In addition to changing the initial composition of the reaction mixture, there is another way to change its structure, the method of introducing inert additives. In our case, in the initial part of the reaction the product in the initial system can be considered as inert additive. As seen from Table 3, the rate of the studied reaction decreases when the reaction product, that is, an inert additive, is added to the initial reaction mixture. Qualitatively, this result can be attributed to the decreasing number of contacts between the reacting solid substances.

For all reactions studied the activation energy was found by the Arrhenius equation. In these calculations we assumed that the initial reaction rate is proportional to the α/t, where time t = 10 min. In this case, to calculate the activation energy we obtain formula (9).

$$E_a = R\cdot[(T_1\cdot T_2)/(T_1 - T_2)]\cdot\ln(\alpha_1/\alpha_2), \quad (9)$$

where T_1, T_2 are the temperatures of the experiment, α_1, α_2 are the initial degrees of conversion at these temperatures, R is the gas constant. The results are shown in Table 6. As can be seen, the activation energy depends strongly and unpredictably on the initial composition of the reaction mixture. The increase in any of the components or the introduction of the reaction product to the initial reaction mixture in all cases leads to a dramatic change in the activation energy. Similar dependences of the activation energy on the initial composition of the reaction mixture we observed previously for irreversible solid-state reactions studied at variable temperature conditions [7]. No explanation of this fact in the framework of the model of the mixture of hard spheres was found.

Thus, the effect of adding phase reactant or product on the state of chemical equilibrium of a reversible solid-state reaction depends on the ability of each phase to change its thermodynamic activity. A phase which retains its individuality in the equilibrium composition practically does not shift the equilibrium when it is added to the mixture. This fact can be used to identify such phases and clarify the mechanism of the reaction and the list of components that produce equilibrium solutions. To account for the non-ideal components in the description of reversible solid-state reactions it can be recommend to apply the regular solution theory, or its more recent variation, that are commonly used to describe the equilibrium in the water–salt systems.

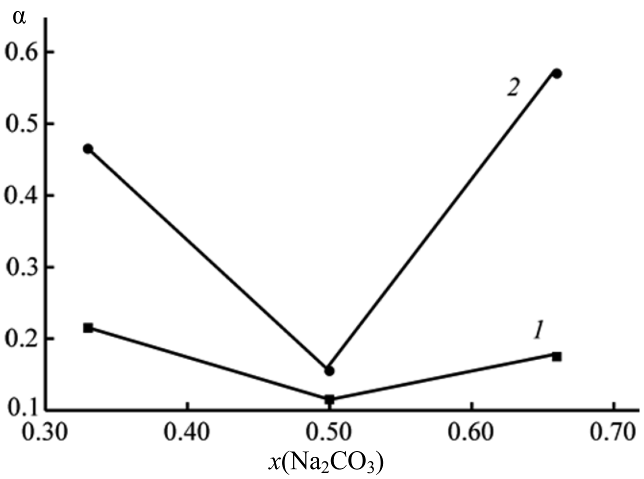

Fig. 3. Dependence of the initial degree of conversion on the initial composition of the mixture for the forward reaction at temperatures of (*1*) 550 and (*2*) 600°C.

EXPERIMENTAL

To determine the composition of the reaction mixture, it was placed in water, mixed well and kept for about 30 min. During this time, the water dissolved Na_2CO_3 and Na_2SO_4, and barium salts $BaCO_3$ and

Table 5. Estimated activation energies of the studied reactions

Forward reaction		Reverse reaction	
Mixture composition	E_a, kJ mol^{-1}	Mixture composition	E_a, kJ mol^{-1}
Na_2CO_3:$BaSO_4$ = 1:1	36	Na_2SO_4:$BaCO_3$ = 1:1	12
Na_2CO_3:$BaSO_4$ = 2:1	138	Na_2SO_4:$BaCO_3$:Na_2CO_3 = 1:1:1	109
Na_2CO_3:$BaSO_4$ = 1:2	92	Na_2SO_4:$BaCO_3$:$BaSO_4$ = 1:1:1	42
Na_2CO_3:$BaSO_4$:$BaCO_3$ = 1:1:1	70	Na_2SO_4:$BaCO_3$ = 1:2	27
Na_2CO_3:$BaSO_4$:Na_2SO_4 = 1:1:1	30	Na_2SO_4:$BaCO_3$ = 2:1	35

$BaSO_4$ remained in the insoluble residue. The aqueous solution was filtered. The Na_2CO_3 content in the filtrate was determined by titration with 0.1 N nitric acid against methyl orange indicator. To determine barium carbonate, the insoluble residue was placed in hydrochloric acid, which dissolves only the barium carbonate. The solution was filtered and the content of Ba^{2+} ions in the filtrate was determined by complexometric titration (ammonia buffer, indicator eriochrome black).

ACKNOWLEDGMENTS

The authors express their sincere thanks to I.I. Kozhina (St. Petersburg State University) for assistance in performing and interpreting the results of XRD.

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