Thermochimica Acta, 68 (1983) 101–111
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

AN APPROACH TO THE KINETICS OF WATER DESORPTION FROM A-ZEOLITES. PART II. RESOLUTION OF THE COMPLEX DEHYDRATION PROCESS TO ELEMENTARY REACTIONS *

VERA DONDUR and DUŠAN VUČELIĆ

Institute of General and Physical Chemistry, Institute of Physical Chemistry, Faculty of Sciences and Mathematics, Belgrade University, P.O. Box 551, Belgrade (Yugoslavia)

(Received 5 April 1983)

ABSTRACT

On the basis of experimental kinetic analysis, it was found that the complex process of water desorption from A-zeolites can be resolved to elementary reactions. Satisfactory agreement was obtained between the calculated and experimental curves.

The Satava–Sestak, Coats–Redfern and Freeman–Carroll methods were applied to determine the kinetic parameters of the elementary reactions. The calculated values of the mathematical constants describe the curves well, but do not represent real kinetic parameters. The activation energies of elementary thermodesorption deviate significantly from the thermodynamic results.

INTRODUCTION

In previous papers [1,2] it was established that water on zeolites exists in several complex forms (three complexes for monovalent counterions, four for bivalent counterions). In such systems, neither isothermal nor non-isothermal kinetic methods can be applied directly [3]. In order to obtain kinetic parameters it is necessary to find relationships between all the complexes. In the most general form, when exchanges exist between all the complexes [4,5], it is difficult to solve the problem mathematically or to obtain all the constants from only one experimental curve. The simplest case is when the thermodesorption processes of all the complexes are independent; then the desorption process can be expressed as the sum of the elementary reactions [6], i.e.

$$-\frac{d\theta}{dt}=\sum_{i=1}^{m} k_i\theta_i^n$$

---

[*] This paper was presented in part at the second European Symposium on Thermal Analysis, Aberdeen, 1981.

where θ is the degree of coverage, m is the number of complexes, θ_i is the degree of coverage of the ith complex, k_i is the rate constant of the ith reaction, and n is the reaction order.

Hence, before any theoretical kinetic analysis, the number of complexes and their interrelationships should be found experimentally.

EXPERIMENTAL

Zeolite powders 4A, 5A and 3A were obtained from Union Carbide. LiA, MgA, CdA and ZnA were prepared by a standard ion-exchange procedure [7]. The instruments used for thermal analysis were the duPont 990 and the Perkin Elmer DSC-1B. Calculation of the kinetic parameters was carried out on PDP-11 and Hewlett Packard 9931 computers. All experimental conditions are the same as in the previous paper [3].

RESULTS AND DISCUSSION

Consecutive water adsorption and desorption on zeolites at different temperatures lead to thermograms with different numbers of peaks. Figure 1 shows the results obtained in the systems NaA–H_2O (Fig. 1a) and MgA–H_2O (Fig. 1b). Adsorption of firmly bound water occurs first, which in thermodesorption corresponds to high temperature peaks. The reaction is very fast at 300 K($t_{1/2} \simeq 1$ min). The formation of this type of bound water occurs even at higher temperatures up to 550 K. It is evident from Fig. 1 that the position of the high temperature peak does not depend on the condition of consecutive adsorption and desorption.

The position of the peaks in lower temperature regions depends on the temperature at which adsorption was carried out and on the initial degree of coverage. However, the most important result is that, even after several days, the shape of the corresponding thermograms remained unchanged for all coverages. That is only possible if equilibrium does not exist between the complexes.

On the basis of this result, an attempt was made to represent the kinetics of water desorption from zeolites by a model of independent parallel reactions. Resolution of the complex experimental DTG curve to the sum of elementary curves was achieved through the usual mathematical procedure using a Gaussian function. The experimental curves were resolved to elementary curves with an error lower than 3%.

Figure 2 shows the results obtained for zeolites with monovalent counterions at maximum degree of coverage. The best fitting was achieved if water

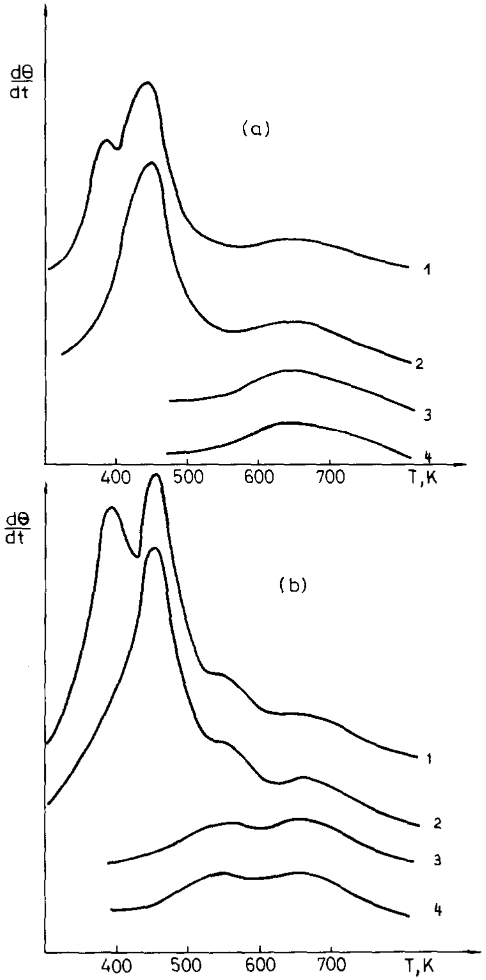

Fig. 1. Thermodesorption of water from (a) NaA; (b) MgA zeolites during consecutive adsorption and desorption DTG (heating rate 10° min^{-1}). 1, Thermodesorption after water adsorption at 300 K; 2, thermodesorption after water adsorption at 400 K; 3, thermodesorption 30 min after adsorption at 500 K; 4, thermodesorption 20 h after adsorption at 500 K.

desorption from KA is represented by two elementary reactions, and from LiA and NaA by three elementary reactions. Satisfactory agreements with experimental results were also attained in the case of zeolites with bivalent cations, see Fig. 3. The complex processes for MgA, CaA, ZnA and CdA zeolites were resolved to four elementary reactions.

The non-isothermal methods of Coats–Redfern [8], Sestak–Satava [9] and Freeman–Carroll [10] were applied to the elementary reactions. The kinetic parameters calculated from the Sestak–Satava method are shown in Table 1.

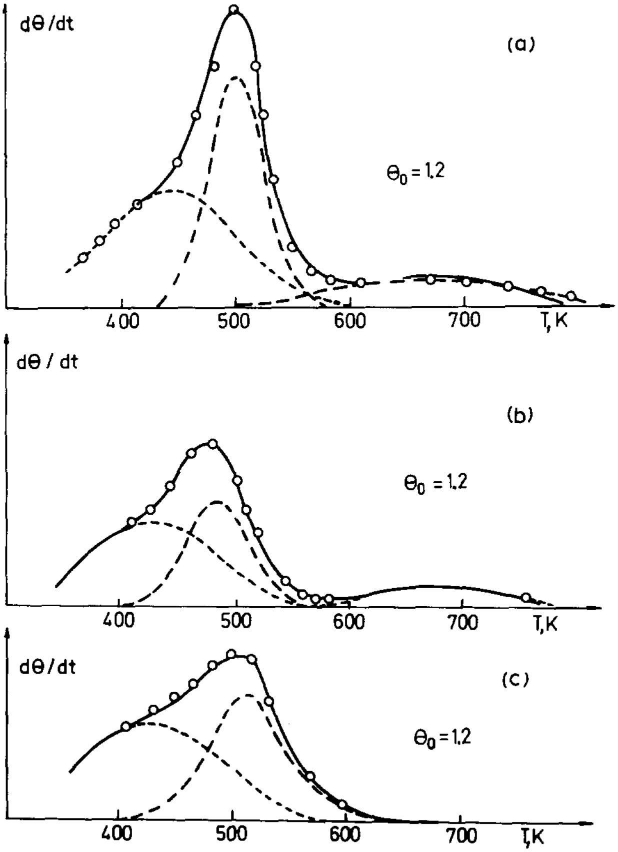

Fig. 2. Resolution of the complex process of water desorption from A-zeolites with monovalent counterions to elementary reactions. (a) LiA; (b) NaA; (c) KA. ———, Experimental DTG curves (heating rate, 32° min^{-1}); - - - - - -, elementary desorption reactions; ○, calculated process.

The elementary reactions are denoted by I, II, II′ and III and correspond to peaks from lower to higher temperatures. The function p(x) was computed using a method suggested by Senum and Yang [11]. In all cases, linearity of the corresponding function is quite high (regression coefficients between 0.999 and 0.996). The results obtained by other methods do not differ by more than 10%.

Although all the results fit very well mathematically, their physicochemical meaning has no sense. The difficulties are listed.

(1) The activation energies of the first processes (I) for the systems NaA, LiA, CaA, CdA and ZnA are lower than the condensation heat of water.

(2) The activation energies of high-temperature processes are lower than the energies for the low-temperature processes.

(3) Agreement between the calculated activation energies and the experimental heat of adsorption is rather poor (see Fig. 6).

TABLE I

Kinetic parameters of elementary desorption processes

Zeolite	Elementary process															
	I				II				II′				III			
	E (kJ mole^{-1})	A (s^{-1})	n	R	E (kJ mole^{-1})	A (s^{-1})	n	R	E (kJ mole^{-1})	A (s^{-1})	n	R	E (kJ mole^{-1})	A s^{-1})	n	R
LiA	27.2	2×10^3	1	0.998	129.5	1.1×10^{11}	2	0.998					75.6	2.6×10^6	2	0.999
NaA	22.9	5×10^3	1	0.999	126.6	2.1×10^{11}	2	0.999					102.0	1.1×10^8	2	0.998
KA	47.2	3.3×10^4	2	0.997	59.3	1.2×10^5	2	0.996								
MgA	90.2	5.8×10^9	2	0.999	58.1	1.3×10^6	1	0.998	29.7	1.1×10^3	1	0.998	33.4	12.5	1	0.999
CaA	25.5	2.3×10^3	1	0.998	49.7	1.5×10^4	1	0.998	154.7	1.3×10^9	2	0.998	34.7	2.5	1	0.999
CdA	33.4	2.3×10^3	1	0.999	56.8	7.7×10^3	1	0.996	138.3	1.3×10^{11}	1	0.998	22.9	5	1	0.999
ZnA	33.0	2.1×10^3	1	0.999	57.7	6.2×10^4	1	0.996	47.2	1.8×10^2	1	0.998	36.8	5	1	0.999

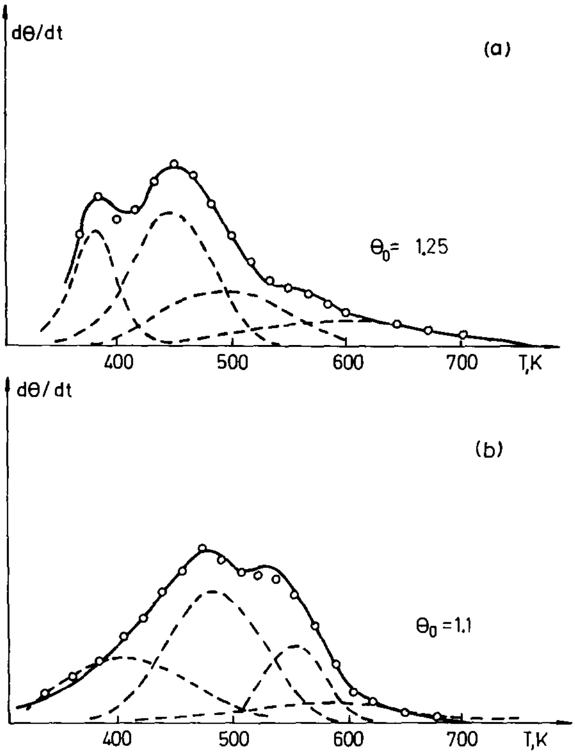

Fig. 3. Resolution of the complex process of water desorption from A-zeolites with bivalent counterions to elementary reactions. (a) MgA; (b) CaA. ———, Experimental DTG curves (heating rate 32° $\min^{-1}$); ○, calculated processes; - - - - - -, calculated elementary reactions.

(4) The values of the pre-exponential factors vary from 10^1 to 10^{11} s^{-1}. Extremely low values were obtained for the pre-exponential factor of zeolites with bivalent cations.

(5) The order of the reaction also varies. In some cases the process corresponds much better to a first-order reaction and in others to a second-order reaction. This is the opposite to the results presented in Part I of the paper [3].

To avoid these difficulties, the computer resolution program was improved by including new physicochemical requirements: all elementary reactions are first order in agreement with the results obtained in the first paper [3]; the activation energy of the elementary reaction is higher or equal to the condensation heat of water; the activation energy of reactions at high temperatures is higher or equal to the activation energy of low-temperature processes; pre-exponential factors follow in the same order.

Figures 4 and 5 show the results of such a resolution when applied to A zeolites with monovalent counterions and bivalent counterions, respectively. It can be seen that the calculated curves deviate significantly from the

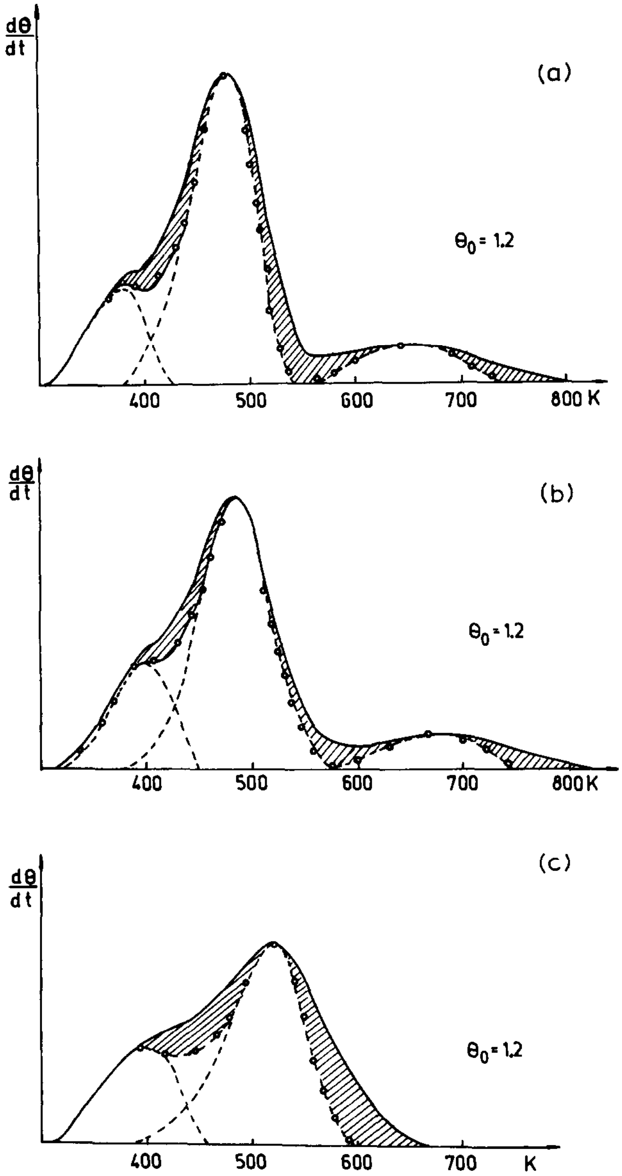

Fig. 4. Resolution of the complex process of water desorption from A-zeolites with monovalent counterions to elementary reactions after introducing additional requirements. (a) LiA; (b) NaA; (c) KA. ————, Experimental DTG curves (heating rate 32° min^{-1}); - - - - - -, calculated elementary reactions; ○, calculated processes. The shaded areas show the difference between experimental and calculated curves.

experimental curves. The deviations are shown by shaded areas. In some cases the deviation is higher than 20%. The kinetic parameters obtained by such a resolution are presented in Table 2. It is evident that after introducing limiting requirements a certain regularity appears between the activation

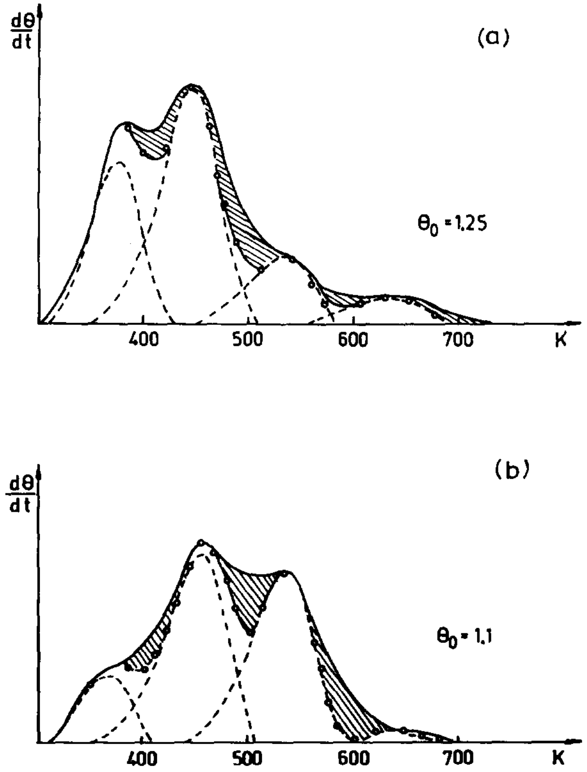

Fig. 5. Resolution of the complex process of water desorption from zeolites with bivalent counterions to elementary reactions after introducing additional requirements. (a) MgA; (b) CaA. ———, Experimental DTG curves (heating rate 32° $\min^{-1}$); ○, calculated processes; - - - - - -, calculated elementary reactions. The shaded areas show the difference between experimental and calculated curves.

energies of particular elementary steps. An energy of about 44 kJ mole^{-1} corresponds to process I, 57 kJ mole^{-1} to process II (depending on the cation), 76 kJ mole^{-1} to process II′ and 71–79 kJ mole^{-1} to process III. Agreement between the calculated activation energies and experimental desorption heats is much better than in the previous case. The calculated differential heat, obtained on the basis of kinetic results for the system NaA–H_2O (Table 2) is presented in Fig. 6. Figure 6 also shows the differential heat of adsorption obtained from ref. 12. The general shape of the calculated curve for the heat of desorption follows the experimental one. This method does not improve the pre-exponential factors; none of them exceed the value of 10^6 s^{-1}. In fact, with regard to pre-exponential factors, this method is even worse than the previous one using a simple Gaussian function without any additional requirements.

In conclusion, mathematically, the model of independent parallel reac-

TABLE 2

Kinetic parameters of elementary desorption processes after including additional requirements

Zeolite	Elementary process							
	I		II		II′		III	
	E (kJ mole^{-1})	*A* (s^{-1})	*E* (kJ mole^{-1})	*A* (s^{-1})	*E* (kJ mole^{-1})	*A* s^{-1})	*E* (kJ mole^{-1})	*A* (s^{-1})
LiA	43.4	3.1×10^4	60.6	5.3×10^5			75.2	2.8×10^6
NaA	43.2	3.0×10^4	58.5	5.5×10^5			79.4	2.0×10^6
KA	45.2	3.3×10^4	56.0	5.8×10^5				
MgA	44.6	3.3×10^4	53.0	6.2×10^5	75.2	7.5×10^5	71.1	2.1×10^6
CaA	44.7	3.1×10^4	57.7	6.0×10^5	77.3	7.3×10^6	75.2	1.8×10^6

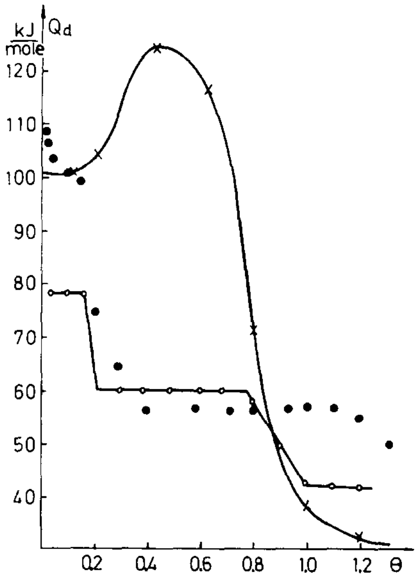

Fig. 6. Dependence of the differential heat of sorption on the degree of coverage in the system NaA–H_2O. ×, Values calculated on the basis of kinetic parameters from Table 1; ○, values calculated on the basis of kinetic parameters from Table 2; ●, experimental differential heat of adsorption [12].

tions can be applied successfully to the thermodesorption of water from zeolites. Both resolution procedures lead to final and constant activation energies and pre-exponential factors. However, they are only mathematical constants of the corresponding differential equations and are more or less in poor agreement with experimental results. Some improvement ought to be expected by varying the activation energies with the degree of coverage within corresponding complexes.

ACKNOWLEDGEMENTS

This research was partially supported by a Republic of Serbia scientific grant. The authors wish to thank D. Fidler for computer assistance.

REFERENCES

1 V. Vučelić, D. Vučelić and M. Šušić, Thermochim. Acta, 8 (1974) 465.
2 V. Dondur, V. Vučelić, D. Vučelić and P. Djurdjević, Thermochim. Acta, 14 (1976) 341.
3 V. Dondur and D. Vučelić, Thermochim. Acta, 68 (1983) 91.
4 S.B. Winterhouse and P. Jewsbury, J. Appl. Phys., 19 (1979) 387.

5 D. Adams, Surf. Sci., 42 (1974) 12.
6 W.L. Winterbotton, Surf. Sci., 36 (1973) 205.
7 R.M. Barrer, W. Buser and W. Guter, Helv. Chim. Acta, 39 (1972) 479.
8 A.W. Coats and J.P. Redfern, Nature (London), 201 (1964) 88.
9 V. Satava and J. Šesták, Anal. Chem., 45 (1973) 154.
10 E.S. Freeman and B. Carroll, J. Phys. Chem., 73 (1977) 751.
11 G.I. Senum and R.T. Yang, J. Therm. Anal., 11 (1977) 445.
12 M.M. Dubinin, A.A. Isirikin, G.U. Rahmatkeriev and V.V. Serpinski, Izv. Akad. Nauk SSSR, Ser. Khim., 10 (1972) 1269.