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STUDY OF THE THERMAL DECOMPOSITION OF SOLIDS IN A FLUIDIZED BED, III

THE INFLUENCE OF THE HUMIDITY UPON THE THERMAL DECOMPOSITION OF DIAMMONIUM HYDROGEN PHOSPHATE UNDER ISOTHERMAL CONDITIONS

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The influence of the air humidity upon the thermal decomposition of diammonium hydrogen phosphate was studied in a fluidized bed, under isothermal conditions. It was found that the increase of the decomposition rate is influenced directly by the partial pressure of the water vapour in the air, and indirectly by the working temperature. The moisture effect is explained by the salt hydrolysis in the water condensed on the grain surface. The energy of activation of the thermal decomposition decreases when the air humidity increases.

Many papers have been published on the thermal decomposition of $(NH_4)_2HPO_4$, either the pure salt or fertilizers containing it [1—7].

Owing to the fact that an important ammonia loss occurs during the drying process in $(NH_4)_2HPO_4$ production, a more detailed study of this problem was necessary.

The ammonia loss in the drying process of $(NH_4)_2HPO_4$ increases with the moisture content of the salt, and with the drying temperature, as proved recently by Kudrashova and co-workers [8]. These authors suggested 50—60° as drying temperature, the obtained salt having a moisture content of 2 wt%.

We earlier studied [9, 10] the thermal decomposition of $(NH_4)_2HPO_4$ under isothermal and non-isothermal conditions, using dried air for fluidization, and we have extended our investigations by using air with different humidities.

Experimental

The apparatus used previously [9] was completed with a device for the saturation of the air with water vapour so that an air flow with different partial pressures of water vapour ($p_{H_2O} = 1.9$; 6.1; 8.5; 14.7; 17.7; 23.2 and 31.2 torr) could be obtained.

For comparison, the thermal decomposition was also run with dried air. The air was dried with anhydrous $CaCl_2$ and P_2O_5. All our experiments were run with 0.061 g of $(NH_4)_2HPO_4$ (p.a. Merck) of 0.15—0.20 mm size. The thermal decomposition of the salt was studied at 69, 78, 89 and 98.3°. Temperatures were chosen at which the decomposition proceeded relatively slowly even in dry air, that is, the kinetics of the decomposition were easy to determine.

As it was outlined earlier [9], at a flow rate of 8 l/h the fluidized bed was found to operate properly. In Tables 1 and 2 it is seen that with the increase of the flow rate above the limiting value of fluidization (in this case from 8 l/h to 12 l/h) the thermal decomposition of the $(NH_4)_2HPO_4$ proceeds in a different way.

Table 1

Decomposition rates for different partial pressures of water vapour at a flow rate of 12 l/h and at different decomposition degrees

p_{H_2O} torr	0.0			14.7			17.7			23.2		31.2	
Temperature, °C	78	89	98.3	89	78	98.3	78	89	98.3	89	98.3	89	98.3
Degree of decomposition, α%	Decomposition rate, $10^2\ \Delta\alpha/\Delta t$												
4.3	0.29	0.91	1.57	0.58	0.98	1.64	0.70	1.21	1.83	1.33	2.50	1.46	2.74
21.3	0.27	0.69	1.38	0.44	0.90	1.48	0.54	1.14	1.63	1.25	1.79	1.30	1.93
42.5	0.26	0.65	1.21	0.42	0.83	1.31	0.52	1.02	1.51	1.10	1.56	1.17	1.63
63.8	0.23	0.55	1.04	0.37	0.68	1.12	0.45	0.81	1.16	0.88	1.23	0.97	1.31

Results and discussion

The degree of decomposition (α) was calculated on the basis of the quantity of NH_3 evolved during the thermal decomposition. When α was plotted versus time, the decomposition curves for different air humidities and different temperatures were obtained (for a flow rate of 8 l/h); these are given in Fig. 1a–c. By means of these curves, the rate of decomposition $\Delta\alpha/\Delta t$ was calculated for different decomposition degrees (Table 2). Subsequently, $\Delta\alpha/\Delta t$ was plotted against p_{H_2O} for different temperatures and at different values of α (Fig. 2a–c). Mathematically, the process can be described for a flow rate of 8 l/h by the following equation: $1 - (1 - \alpha)^{1/3} = kt$, where α is the decomposition degree and t is the time. $1 - (1 - \alpha)^{1/3}$ was plotted against time, and from the slopes of the lines the rate constant k was calculated. Subsequently, the Arrhenius law $k = A \cdot \exp(-E/RT)$ was taken into account and the $\log k$ vs. $1/T$ plot was prepared; from the slopes of the lines the activation energy was calculated. The experimental data obtained for various temperatures and different p_{H_2O} values are given in Table 3. By using the least squares method, the confidence limits for the

Table 2

Decomposition rates for different partial pressures of water vapour at a flow rate of 8 l/h and different decomposition degrees

p_{H_2O} torr	0.0			1.9			6.1			8.5			14.7			17.7		
Temperature, °C	69	78	89	69	78	89	69	78	89	69	78	89	69	78	89	69	78	89
Degree of decomposition, α %	Decomposition rate, $10^3\ \Delta\alpha/\Delta t$																	
4.3	1.34	2.88	6.33	1.62	3.08	6.62	2.10	3.70	7.25	2.40	4.05	7.50	2.53	4.94	8.50	2.72	5.36	9.96
21.3	1.11	2.31	5.16	1.43	2.49	5.52	1.94	3.18	6.01	2.20	3.57	6.42	2.24	4.40	8.23	2.32	4.85	8.74
42.5	0.94	1.93	4.49	1.19	2.09	4.68	1.67	2.71	5.30	1.73	3.05	5.75	1.84	3.94	7.13	2.09	4.35	7.42
63.8	0.70	1.45	3.01	0.87	1.57	3.37	1.24	1.98	3.59	1.40	2.16	4.12	1.50	2.54	4.79	1.60	2.85	6.38
85.0	0.48	0.88	2.03	0.51	0.90	2.17	0.68	1.21	2.44	0.74	1.36	2.64	0.80	1.64	3.31	0.84	1.71	3.44

activation energy were calculated. It was ascertained that the activation energy decreases when the humidity of the air increases.

No kinetic equation was found suitable for the description of the thermal decomposition process of $(NH_4)_2HPO_4$ when a flow rate of air of 12 l/h was used.

From experimental data, the following conclusions were drawn for a flow rate of 8 l/h:

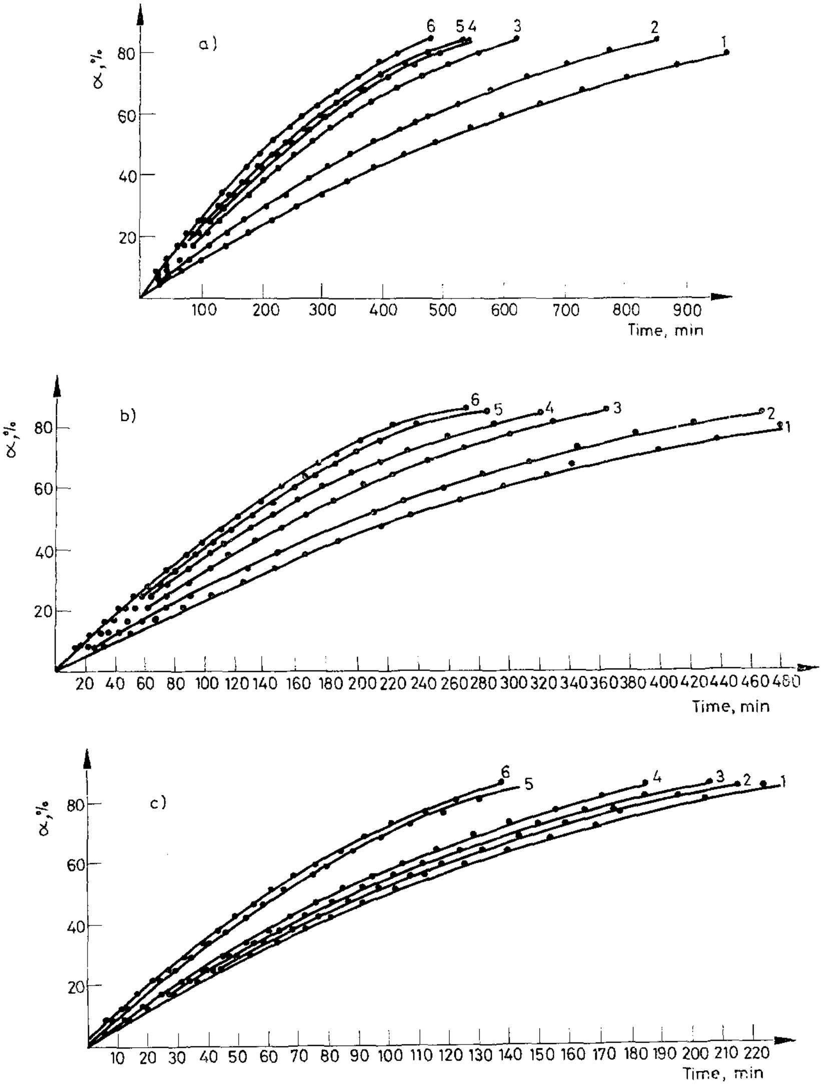

Fig. 1. Effect of the partial pressure of water vapour on the thermal decomposition; air flow rate 8 l/h. a) 69°; b) 78°; c) 89°. Curve 1: 0.0 torr; 2: 1.9 torr; 3: 6.1 torr; 4: 8.5 torr; 5: 14.7 torr; 6: 17.7 torr

1. The maximum decomposition rate is already achieved at the beginning of the thermal decomposition reaction.

2. When dried air is used, the values of $\Delta\alpha/\Delta t$ (Table 2 and Fig. 2a–c) are always the lowest. The decomposition rate increases with increasing air humidity.

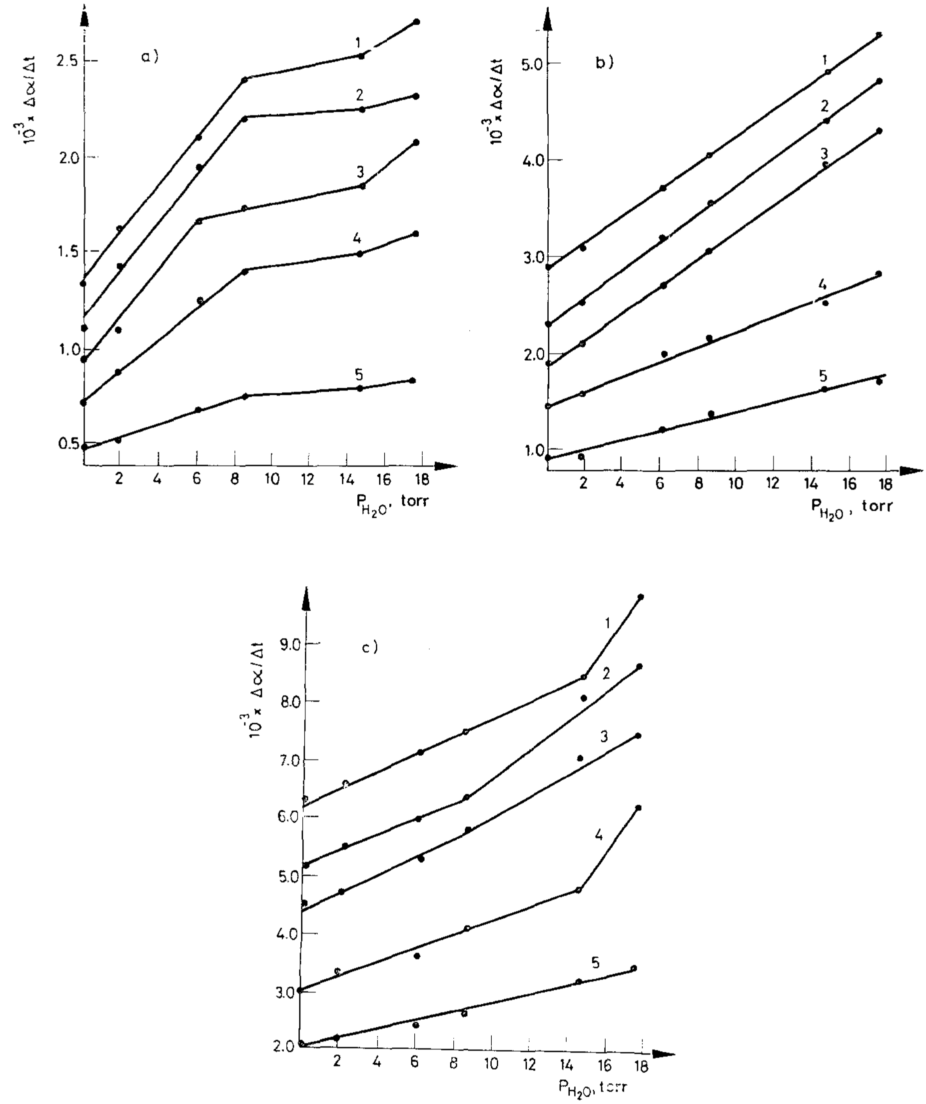

Fig. 2. Effect of the partial pressure of water vapour on the decomposition rate. a) 69°; b) 78°; c) 89°. Curve 1: $\alpha = 4.3\%$; 2: $\alpha = 21.3\%$; 3: $\alpha = 42.5\%$; 4: $\alpha = 63.8\%$; 5: $\alpha = 85\%$ The values of the ordinates are $10^3 \times \Delta\alpha/\Delta t$.

Table 3

Rate constants and activation energies for different partial pressures of water vapour at a flow rate of 8 l/h

Temperature °C	Partial pressure of water vapour, p_{H_2O} torr					
	0.0	1.9	6.1	8.5	14.7	17.7
	$10^4\,k$ (min^{-1})					
69	3.96	5.62	7.81	8.50	8.82	9.89
78	8.76	11.00	13.10	14.80	16.10	18.10
89	20.30	21.80	23.00	24.30	32.60	34.00
$E_{act.}$ kcal/mol	20.2 ± 0.1	16.8 ± 0.2	—	—	15.8 ± 0.1	15.3 ± 0.1

$(NH_4)_2HPO_4$ agglomerated at lower temperatures (78°) at above 17.7 torr p_{H_2O} in the air, and no kinetic study was possible beyond this limit.

3. A given p_{H_2O} has different effects upon the value of $\Delta\alpha/\Delta t$ at different temperatures. At lower temperatures, the increase of p_{H_2O} causes a more significant increase of the decomposition rate. Table 4 gives the average values of the ratio obtained by dividing the time in the case of dried air by the time at $p_{H_2O} = 14.7$ torr, for identical values of α. For example, at 69° this coefficient is 2.03, while at 98.3° it is only 1.05.

Table 4

Average of the ratios time of decomposition in dry air/time of decomposition in moist air, at different partial pressures of water vapour

Temperature °C	$\frac{\text{time of decomp. at } p_{H_2O} = 0.0 \text{ torr}}{\text{time of decomp. at } p_{H_2O} = 14.7 \text{ torr}}$	$\frac{\text{time of decomp. at } p_{H_2O} = 0.0 \text{ torr}}{\text{time of decomp. at } p_{H_2O} = 17.7 \text{ torr}}$
69.0	2.03	2.26
78.0	1.88	1.99
89.0	1.57	1.67
98.3	1.05	1.14

4. The air humidity influences the entire thermal decomposition reaction uniformly. This is reflected by the constant values of the ratio $\text{time}_{(\text{dried air})}/\text{time}_{(\text{moist air})}$ for different α values. The values of this ratio are given in Table 5.

1. $\Delta\alpha/\Delta t$ has higher values than for 8 l/h, under otherwise identical conditions (temperature and p_{H_2O}).

2. The decomposition rate increases with the increase of p_{H_2O}, but this increase is not linear. The influence of p_{H_2O} is more significant between 14.7 and 23.2 torr than up to 14.7 torr.

3. At this flow rate the particles begin to crumble. Due to this factor (the change of particle size vs. time), no known kinetic equation was found suitable for the

Table 5

The values of the ratios time of decomposition in dry air/time of decomposition in moist air, at different degrees of decomposition and different temperatures

Degree of thermal decomposition, α	$\frac{\text{time of decomposition at } p_{H_2O} = 0.0 \text{ torr}}{\text{time of decomposition at } p_{H_2O} = 14.7 \text{ torr}}$		
	69°C	78°C	89°C
4.2	1.71	1.64	1.55
8.5	2.09	1.80	1.53
17.0	2.07	1.79	1.57
21.3	2.05	1.79	1.59
25.0	1.99	1.82	1.58
42.5	1.97	1.79	1.59
47.0	2.02	1.92	1.59
59.5	2.02	1.93	1.56
63.8	2.01	1.68	1.58
68.0	1.99	1.88	1.58
81.0	2.10	1.84	1.54

description of the thermal decomposition of $(NH_4)_2HPO_4$ when a flow rate of air of 12 l/h was used.

In connection with the influence of the humidity upon the thermal decomposition of $(NH_4)_2HPO_4$ in the solid state, the following mechanism is possible: The water vapour is condensed on the grain surface. For a known size of sample, the amount of water condensed is proportional to p_{H_2O} and inversely proportional to the temperature. The condensation of water on the grain surface was proved by water determination of the air in front of and behind the fluidized bed, using the Karl-Fischer method. The water content in the air was found to decrease on passing through the fluidized bed. The hydrolysis of $(NH_4)_2HPO_4$ took place in the water film condensed on the grain surface.

$$(NH_4)_2HPO_4 + H_2O \rightleftharpoons NH_4H_2PO_4 + [NH_4OH]; \quad [NH_4OH] \rightleftharpoons NH_3 + H_2O$$

Thus, the water promotes the thermal decomposition by weakening the chemical bonds within the ammonium ions resulting on the reaction surface in the hydrolysis. As the amount of condensed water increases, the thermal decomposition becomes faster, the equilibrium being shifted more and more to the right. The constant values of the ratio: $\text{time}_{(\text{dried air})}/\text{time}_{(\text{moist air})}$ (Table 5) proved that the thickness of the water film remained unchanged, though the interface moved into the depth of the grain. Hence the water resulting from the decomposition of ammonium hydroxide is retained on the reaction interface, the quantity of the water being proportionally reduced only as a result of the diminishing of the area of the reaction interface. Owing to this fact, the maximum rate of the thermal decomposition is achieved at the beginning when the reaction area has a maximum value.

As the area decreases, the decomposition rate also decreases so that the kinetic equation elaborated on the basis of the contracting sphere model: $1 - (1 - \alpha)^{1/3} = kt$, remains valid throughout this process. Its validity is not affected by whether the air is dry or moist, and consequently, the kinetically essential step of the process consists in the weakening of the bonds within the ammonium ion, a phenomenon which is favoured by the presence of condensed water. At higher temperatures, however, the amount of water in the condensed state on the interface is reduced, so that the effect of the air humidity is reduced as well. This is the explanation for the fact that the influence of the air humidity is almost completely reduced (Table 4) even at $p_{H_2O} = 14.7$ torr when temperature is as high as 98.3°.

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Résumé — On a étudié l'influence de l'humidité atmosphérique sur la décomposition thermique de $(NH_4)_2HPO_4$ en lit fluidisé, en conditions isothermes. La pression partielle de la vapeur d'eau dans l'air intervient directement sur l'augmentation de la vitesse de décomposition et exerce une action indirecte sur la température de travail. On a expliqué l'effet de l'humidité par l'hydrolyse du sel dans l'eau condensée à la surface des grains. La valeur de l'énergie d'activation de la décomposition thermique diminue quand l'humidité atmosphérique augmente.

Zusammenfassung — Der Einfluß der Luftfeuchtigkeit auf die thermische Zersetzung des Diammoniumhydrogenphosphats wurde in fluidisiertem Bett unter isothermen Verhältnissen studiert. Die Zunahme der Zersetzungsgeschwindigkeit war direkt proportional dem partialen Wasserdampfdruck in der Luft und indirekt proportional der Arbeitstemperatur. Diese Wirkung wird durch Salzhydrolyse in dem kondensierten Wasser an der Kernoberfläche erklärt. Die Aktivierungsenergie der thermischen Zersetzung nimmt mit zunehmendem Feuchtigkeitsgehalt ab.

Резюме — Исследовано влияние влажности воздуха на термораспад гидрофосфата аммония в кипящем слое при изотермических условиях. Обнаружено, что парциальное давление воды, находящейся в воздухе, непосредственно влияет на увеличение скорости распада, влияние же температуры при эксперименте более посредственно. Эффект увлажнения объяснен гидролизом соли в воде, конденсированной на поверхности зерна.