

## STUDY OF THE THERMAL DECOMPOSITION OF SOLIDS IN A FLUIDIZED BED, II

THERMAL DECOMPOSITION WITH PROGRAMMED TEMPERATURE  
OF DIAMMONIUM HYDROGEN PHOSPHATE\*

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In order to eliminate the errors of the TG method with a static layer, and to determine the influence of the heating rate, the composition of the carrier gas and the particle size of the solids, a method of thermal gas evolution from a fluidized bed (FTGE) with continuous and linear increase of temperature was worked out and the thermal decomposition of diammonium hydrogen phosphate was followed. This method gives reproducible results and makes possible the determination of the apparent activation energies and kinetic parameters.

During recent years, thermoanalytical methods have often been used to study the thermal decomposition of solids. A number of TG, DTA and thermal gas-volumetric apparatuses have been constructed. There are many reports of TG data being used to assess kinetic parameters (order of reaction, activation energy, etc.).

In the study of the thermal decomposition of solids, even in the most simple case

$$A_{(\text{solid})} = B_{(\text{solid})} + C_{(\text{gas})}$$

two main problems occur: the first is connected with the process of decomposition (cleavage of chemical bonds, destruction of the initial crystalline lattice, formation of a new lattice, and diffusion of the gaseous product), and the second problem is connected with the following and control of the thermal decomposition. Consequently, the thermal process of decomposition will be influenced by the size of the solid particles, the diffusion of the gas, the thickness of the solid layer and the heating rate.

As a rule in the TG apparatuses used so far, the finely divided solid is put into a metal, ceramic, quartz, or other crucible in a fixed layer, more or less compactly. The temperature gradient in this fixed layer is variable, depending on the thermal conductivity of the solid, on the material of the crucible, and on the composition of the furnace atmosphere. The degree of compactness and thickness of the layer will influence the removal of the gas produced in the interior. The gaseous product is more easily removed from the surface of the layer than

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from inside. Due to this fact, the statistical probability of the thermal decomposition of a solid particle in a static layer is not the same as in a non-static layer. Consequently, the TG data will influence more or less the determination of the correct kinetic parameters.

In order to eliminate the errors of the TG methods and to determine the influence of the particle size of the sample, the rate of temperature increase and the composition of the carrier gas, the method of thermal gas evolution from a fluidized bed (FTGE) with continuous and linear increase of the temperature was worked out.

### Experimental

Diammonium hydrogen phosphate p.a., E. Merck (Darmstadt, Germany), was used as model solid. The following system was studied and is discussed in detail:



In all experiments 0.061 g salt was used. The following particle sizes were used: 0.15–0.20 mm; 0.25–0.30 mm; 0.40–0.43 mm.

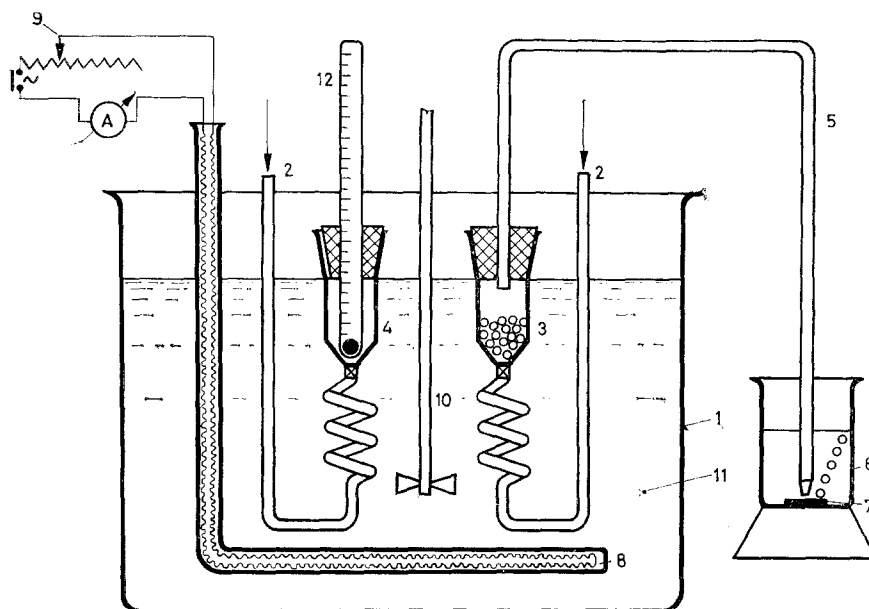


Fig. 1. Scheme of the apparatus. 1. Razotherm glass vessel with asbestos insulation; 2. Tubes for passing carrier gas; 3. Phial with fluidized  $(\text{NH}_4)_2\text{HPO}_4$ ; 4. Phial identical with phial 3; 5. Connection tube; 6. Titration glass with acid; 7. Magnetic stirrer; 8. Heater; 9. Autotransformer; 10. Stirrer; 11. Oil bath; 12. Thermometer

The scheme of the apparatus is shown in Fig. 1. The dried carrier gas is passed through a tube at a constant rate and is heated to the temperature of the oil bath; it then passes through the phial where it produces the fluidized bed. Ammonia evolved during the decomposition of the salt is trapped in 0.01  $N$   $H_2SO_4$  solution. The degree of decomposition ( $\alpha$ ) as a function of the temperature increase is determined by measuring the time necessary to neutralize a known quantity of acid. A 1 : 1 mixture of methyl red and methylene blue is used as indicator. The constant heating rate is ensured by heating the oil bath with an electrical resistance regulated by an autotransformer. The oil bath is stirred. The temperature in the fluidized bed is measured indirectly. Phials 3 and 4 are similar in shape and made of heat-resistant glass. The thermometer is placed in phial 4. The carrier gas passes through phial 4 with the same flow rate as through phial 3. Before the experiments, it was ascertained that the heating rate is the same in both phials. A continuous increase of the temperature in the fluidized bed is possible with the heating system applied.

## Results

With the method described the influence of the following factors was studied: particle size, heating rate, flow rate, and composition of carrier gas. The thermal decomposition is characterized by the temperature  $T_i$  at which  $\alpha = 0.2\%$  (the first temperature observed) and  $T_{max}$  at which the rate of decomposition is maximum.

The mathematical treatment of the experimental data was performed with the method elaborated by Zsako [1]. It was established by a trial-and-error pro-

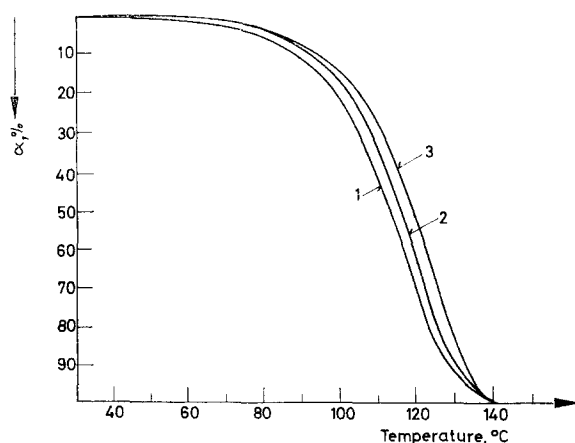


Fig. 2. Effect of the particle size. Heating rate: 1 °C/min; Carrier gas: air; Flow rate: 12 l/h  
1. 0.15–0.20 mm; 2. 0.25–0.30 mm; 3. 0.40–0.43 mm

cedure that our data are best represented by equations of the type:

$$\frac{d\alpha}{dt} = k(1 - \alpha)^b$$

where  $k = f(T)$  and  $b$  is equal to  $2/3$  and  $1$ . Zsako's method enabled us to compute the apparent activation energy as well as the standard deviations ( $\delta$ ) which give a quantitative measure of the agreement between the postulated kinetic equation and the experimental data.

*Effect of the particle size.* The experimental data for three sizes are given in Fig. 2 and Table 1.  $T_i$  and  $T_{max}$  increase with increasing particle size of the sample.

Table 1

Heating rate, °C/min	1					
Carrier gas	Air					
Flow rate, l/h	12					
Particle size, mm	0.15–0.20		0.25–0.30		0.40–0.43	
$T_i$ , °C	37		39		43	
$T_{max}$ , °C	116		120		124	
Apparent order of reaction, $b$	1	2/3	1	2/3	1	2/3
Standard deviation, $\delta$	0.007	0.011	0.020	0.013	0.013	0.032
$E$ , kcal/mole	22.0	19.4	22.2	21.2	23.6	21.4

For an apparently first order reaction, the apparent activation energy  $E$  is less than 22 kcal/mole, and for a  $2/3$  order less than 21 kcal/mole.

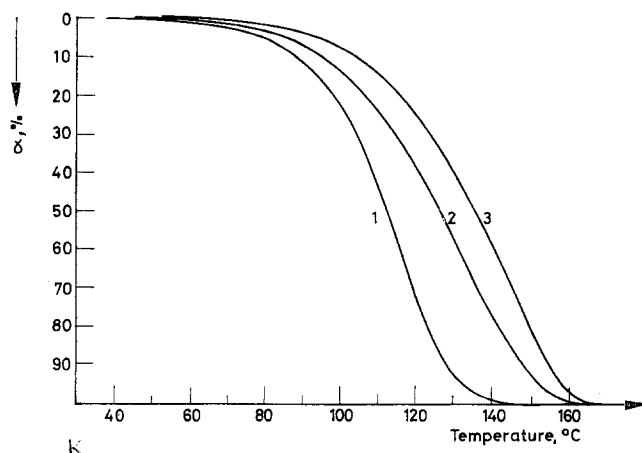


Fig. 3. Effect of the heating rate. Particle size: 0.15–0.20 mm; Carrier gas: air; Flow rate: 12 l/h. 1. 1 °C/min; 2. 2.5 °C/min; 3. 5.3 °C/min

*Effect of the heating rate.* The influence of the heating rate was studied using a particle size of 0.15–0.25 mm and dried air as carrier gas at a flow rate of 12 l/hour. The following heating rates were applied: 1, 2.5 and 5.3°/min.  $T_i$  and  $T_{max}$  increase with increasing heating rate. The activation energy decreases with the increase of the heating rate. The experimental data are given in Table 2 and

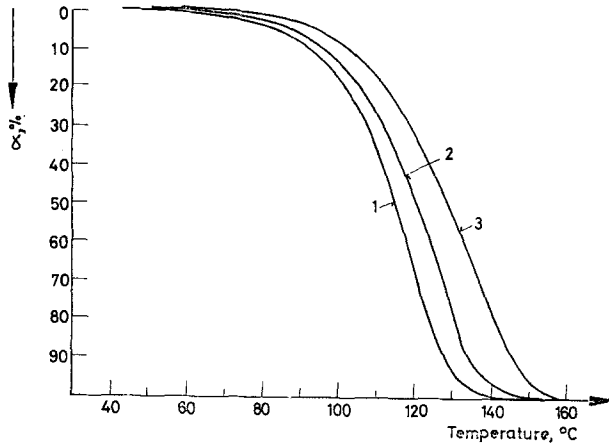


Fig. 4. Effect of the heating rate. Particle size: 0.25–0.30 mm; Carrier gas: air; Flow rate: 12 l/h. 1. 1° C/min; 2. 1.75 °C/min; 3. 2.5 °C/min

Fig. 3. The same conclusions were drawn with a particle size of 0.25–0.30 mm. The experimental data are given in Table 2 and Fig. 4. It is clear from this table that when particles of two different sizes are heated at the same rate, the differences between the values  $E$  are not significant.

Table 2

Carrier gas	Air									
	0.15–0.20				12		0.25–0.30			
Flow rate, l/h	12									
Particle size, mm	0.15–0.20									
Heating rate, °C/min	1		2.5		5.3		1		2.5	
$T_i$ , °C	37.0		44.0		52.0		39.0		53.0	
$T_{max}$ , °C	116.0		129.0		134.5		120.0		136.0	
Apparent order of reaction, $b$	1	2/3	1	2/3	1	2/3	1	2/3	1	2/3
Standard deviation, $\delta$	0.007	0.011	0.015	0.003	0.016	0.019	0.020	0.012	0.021	0.018
$E$ , kcal/mole	22.0	19.4	19.8	18.6	17.8	17.0	22.2	21.2	20.8	18.4

*Effect of the flow rate of the carrier gas.* In order to follow the effect of the flow rate of carrier gas, a particle size of 0.15–0.20 mm, a heating rate of 1°/min, and dried air were used. At a flow rate of 8 l/h the fluidized bed was found to operate properly. At a flow rate of only 4 l/h the layer showed a little movement and at 2.5 l/h was nearly static. In Table 3 and Fig. 5 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)  $T_i$  and  $T_{max}$  exhibit no significant differences. In other cases, when a flow rate less than the limiting value of fluidization was used,  $T_i$  and  $T_{max}$  increased significantly. The equation was found to be valid for a first and 2/3 order reaction. In the first case, the apparent  $E$  is less than 21 kcal/mole, and for the second less than 19 kcal/mole.

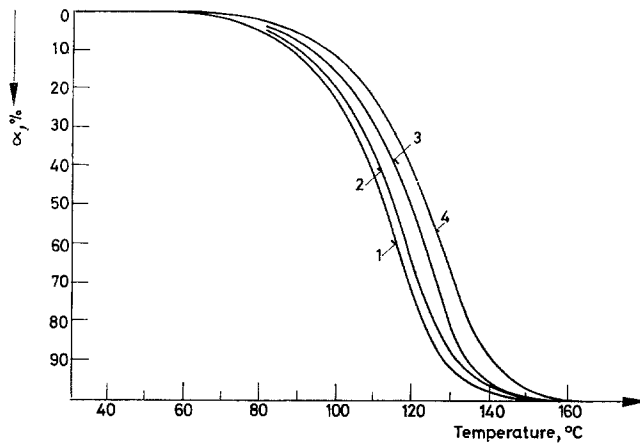


Fig. 5. Effect of the flow rate of the carrier gas. Particle size: 0.15–0.20 mm; Carrier gas: air; Flow rate: 1. 12 l/h; 2. 8 l/h; 3. 4 l/h; 4. 2.6 l/h

Table 3

Heating rate, °C/min	1							
	Air							
Carrier gas	fluidization		fluidization		moving		static	
Layer state	12		8		4		2.6	
Flow rate, l/h	37.0		37.0		48.0		50.6	
$T_i$ , °C	116.0		117.8		124.0		129.0	
$T_{max}$ , °C								
Apparent order of reaction, $b$	1	2/3	1	2/3	1	2/3	1	2/3
Standard deviation, $\delta$	0.007	0.011	0.011	0.005	0.018	0.007	0.0085	0.0077
$E$ , kcal/mole	22.0	19.4	20.8	18.2	21.4	19.4	20.4	19.0

*Effect of the carrier gas.* It may be seen from Table 4 and Fig. 6 that when the flow rate is above the limiting value of fluidization,  $T_i$  and  $T_{\max}$  do not change significantly on changing the carrier gas from air to hydrogen.

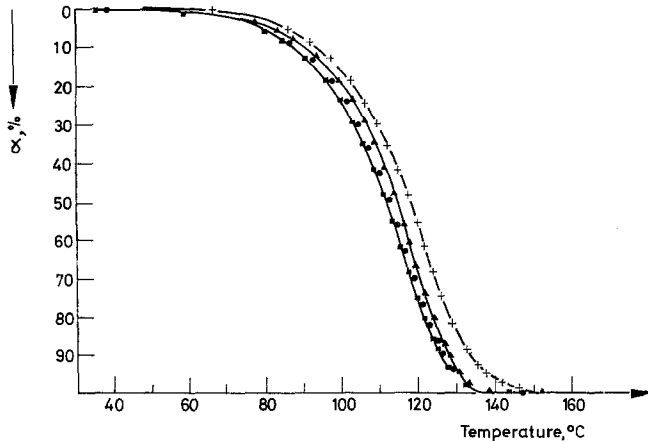


Fig. 6. Effect of the composition of the carrier gas. Particle size: 0.15–0.20 mm; Flow rate: 12 l/h and 4 l/h; Heating rate: 1 °C/min. 1. Hydrogen (12 l/h) ■; 2. Air (12 l/h) ●; 3. Hydrogen (4 l/h) ▲; 4. Air (4 l/h) +

Table 4

Heating rate, °C/min	1		4	
	Hydrogen	Air	Hydrogen	Air
Carrier gas				
Flow rate, l/h	12		4	
$T_i$ , °C	36.0	37.0	40.0	48.0
$T_{\max}$ , °C	115.0	116.0	119.7	124.0
Apparent order of reaction, $b$	2/3	2/3	2/3	2/3
Standard deviation, $\delta$	0.0129	0.011	0.0041	0.0048
$E$ , kcal/mole	19.0	19.4	20.4	19.4

For a very small flow rate, for example 4 l/h, with only some movement of the layer, the influence of the composition of the carrier gas is more significant.  $T_i$  and  $T_{\max}$  decrease when hydrogen is used. With hydrogen only the equation of the 2/3 order is valid. The apparent  $E$  is less than 19 kcal/mole.

### Discussion

A comparison of our data with those of other researchers [2–5] (Table 5) shows that  $T_i$  and  $T_{\max}$  decrease when a fluidized bed is used. The differences are marked in some cases.

Table 5

Method	FTGE	TG [2]	TG [3]	TG [4, 5]
Layer state	fluidization	static	static	static
Particle size, mm	0.15–0.20	not indicated	0.15	not indicated
Heating rate, °C/min	5.3	5.0	4.0	not indicated
$T_b$ , °C	52.0	100	50.0	70 [4]
$T_{max}$ , °C	134.5	150.0	140.0	152.0 [5]

From the considerations presented above it is seen that the thermal decomposition of solids is influenced by a number of factors. Their effects are not equivalent. In order to illustrate the effects of the studied factors, all the experimental data are given in Table 6.

Table 6

Particle size, mm	Carrier gas	Flow rate, l/h	Heating rate, °C/min	Temperature for $\alpha = 50\%$	$E$ , kcal/mole	
					$b = 1$	$b = 2/3$
0.15–0.20	hydrogen	12	1	110.8	—	19.0
0.15–0.20	air	12	1	111.4	22.0	19.4
0.15–0.20	air	8	1	114.6	21.4	18.2
0.15–0.20	hydrogen	4	1	114.6	—	20.4
0.25–0.30	air	12	1	114.8	22.2	21.2
0.15–0.20	air	4	1	118.2	20.8	19.4
0.40–0.43	air	12	1	118.8	23.6	21.4
0.25–0.30	air	12	1.75	120.6	23.6	20.8
0.15–0.20	air	12	2.5	122.5	19.8	18.6
0.15–0.20	air	2.6	1	122.5	20.4	19.0
0.25–0.30	air	12	2.5	129.2	20.8	18.4
0.15–0.20	air	12	5.3	135.8	17.8	17.8

Table 6 shows that the flow rate of the gas, the particle size of the solid, and the composition of the carrier gas have only small effects upon the thermal decomposition of the solid. The most important effect upon the thermal decomposition is that of the heating rate, but the absence of fluidization is also of great significance. The differences in the temperatures of reaching  $\alpha = 50\%$  at a 1°/min heating rate with a good fluidized bed are only 6–7°. The temperature difference increases to 11° and to 24.4° for 2.5°/min and 5.3°/min heating rates, respectively. In order to obtain reproducible data it is necessary to control the heating rate and produce a good fluidized bed. This was confirmed by the kinetic parameters obtained from our  $\alpha = f(T)$  curves. The apparent activation energy is strongly influenced by the heating rate and decreases with its increase. This situation is



Table 7

Layer state	Fluidization		
	0.15—0.20	0.25—0.30	0.40—0.43
Particle size, mm			
Carrier gas		Air	
$E_{\text{isothermal}}$ , kcal/mole	19.2	22.2	23.1
$E_{\text{FTGE}}$ , kcal/mole	19.4	21.2	21.4
Apparent order of reaction, $b$	2/3	2/3	2/3

similar to a departure from isothermal conditions. In our opinion, by using a very low heating rate one can approach isothermal conditions, so the apparent activation energies computed from  $\alpha = f(T)$  and  $\alpha = f(t)$  [6] are nearly the same. In Table 7 are given the apparent activation energies under isothermal conditions and with continuous rise of temperature. The data given in Table 7 support our conclusions. The values of  $E$  are less with greater particle sizes (under non-isothermal conditions). This supports our view and also the applicability of the 2/3 order kinetic equation. This equation was deduced for the contracting sphere model according to which the thermal decomposition of solids proceeds from the outer part of a grain towards the inside, after the heat front, simultaneously with the diffusion of the gaseous product from within towards the outer part.

### Conclusions

1. The method of thermal gas evolution from a fluidized bed with continuous and linear increase of temperature made possible to follow the thermal decomposition of finely divided solids.
2. This method gave reproducible data and made possible the exact determination of  $T_i$  and  $T_{\text{max}}$  when the particle size, the flow rate of the gas and the heating rate were constant.
3. The apparent activation energies and kinetic parameters of the equations valid for the total process were computed from  $\alpha = f(T)$  curves.
4. The method cannot be used for solids which agglomerate or melt.
5. The method was used in the 20–160° range. This range may be extended by using another apparatus.

### References

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RÉSUMÉ — Dans le but d'éliminer les erreurs des procédés thermogravimétriques avec couches fixes, et de mettre en évidence l'influence de la vitesse d'échauffement de la composition du gaz porteur et de la dimension des solides, on a développé une méthode d'analyse des gaz dégagés, avec lit fluidifié et élévation de la température continue et linéaire. On a suivi ainsi la décomposition thermique de  $(\text{NH}_4)_2\text{HPO}_4$ . Cette méthode donne des résultats reproductibles et rend possible la détermination des énergies d'activation apparentes et des paramètres cinétiques.

ZUSAMMENFASSUNG — Um die Fehler der TG Methode unter fixierten Verhältnissen zu eliminieren, den Einfluß der Temperaturerhöhung, der Zusammensetzung des Trägergases und des Ausmaßes der Festkörper zu klären, wurde eine thermogasanalytische Methode im fluidisierten Bett (FTGE) mit kontinuierlichem und linearem Temperaturanstieg entwickelt und die thermische Zersetzung des Diammonium-biphosphates verfolgt. Man erhielt mit dieser Methode reproduzierbare Ergebnisse. Sie ist zur Bestimmung der scheinbaren Aktivierungsenergien und kinetischer Parameter geeignet.

Резюме. — Для исключения ошибок метода ТГ в неподвижном слое, выяснения влияния скорости нагрева и состава газа носителя, а также навески твердого образца разработан новый метод в кипящем слое с постоянным и линейным повышением температуры. Этим методом изучен термораспад двухзамещенного фосфата аммиака. Метод дает воспроизводимые результаты, что делает возможным определение кажущейся энергии активации и кинетических параметров.