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STUDY ON THE THERMAL DECOMPOSITION OF SOLIDS IN FLUIDIZED BED

I. ISOTHERMAL DECOMPOSITION OF DIAMMONIUM HYDROGENPHOSPHATE

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Reliable thermodynamic parameters for the thermal decomposition of diammonium hydrogenphosphate [$(NH_4)_2HPO_4$] may be obtained using a fluidized bed. For the same size of particle, at the same temperature, but for different carrier gases, the rate constant and activation energy increase in the following order: air, methane, hydrogen. For the same carrier gas (air) the rate constant increases when the particle size decreases.

It is well known that diammonium hydrogenphosphate is a constituent of fertilizers. The thermal decomposition of pure diammonium hydrogenphosphate and of fertilizers containing this salt has been studied [1–6] but no kinetic study of the decomposition has been made so far. One of the major problems associated with the kinetics of solid state reactions is the evaluation of activation energies and related parameters for clearly identified processes beginning from the initial portion of nucleation, through the various intermediate phases to the final stages of decomposition [7].

In order to study the thermal decomposition of $(NH_4)_2HPO_4$, the isothermal method in a fluidized bed has been utilized. This method has been elaborated by Kröbl [8] in order to study the thermal decomposition of cobalt (III)-amino complexes. An outline of the apparatus is shown in Fig. 1.

Air, methane and hydrogen were used in order to study the influence of carrier gas upon kinetic parameters. The pressure of the gases was constant and equal in every case. The flow rate was 8 l/h. Ammonia evolved during the decomposition of $(NH_4)_2HPO_4$ was trapped in a 0.01 N H_2SO_4 solution. A 1 : 1 mixture of methyl red with methylene blue was used as indicator.

In order to study the influence of particle size upon kinetic parameters, we always worked with 0.0611 g $(NH_4)_2HPO_4$ of the following sizes: 0.10–0.07 mm; 0.20–0.15 mm; 0.30–0.25 mm and 0.40–0.43 mm. That such small quantities are required is a fact of considerable importance in the study of the thermal decomposition.

An equation was sought which well describes the kinetics of thermal decomposition. Taking into account the complexity of the process, there is little chance of finding a general equation capable of describing the kinetics of all thermal decomposition reactions, especially in the case when the kinetics vary during the process [9].

A fluidized bed was quite useful in the studies because of the temperature homogeneity and uniform gas diffusion and desorption on the sample surface [10]. The partial pressure of ammonia on the surface of the particles was reduced remarkably, because the particles were surrounded by a large quantity of gas; the situation is thus like that in high vacuum. In this way diffusion is hindered and competitive reactions do not occur so that the thermal decomposition is simpler.

In our work on the thermal decomposition of $(NH_4)_2HPO_4$ we used data obtained by Deschanvres and Nouet [11] in a study of the thermal decomposition

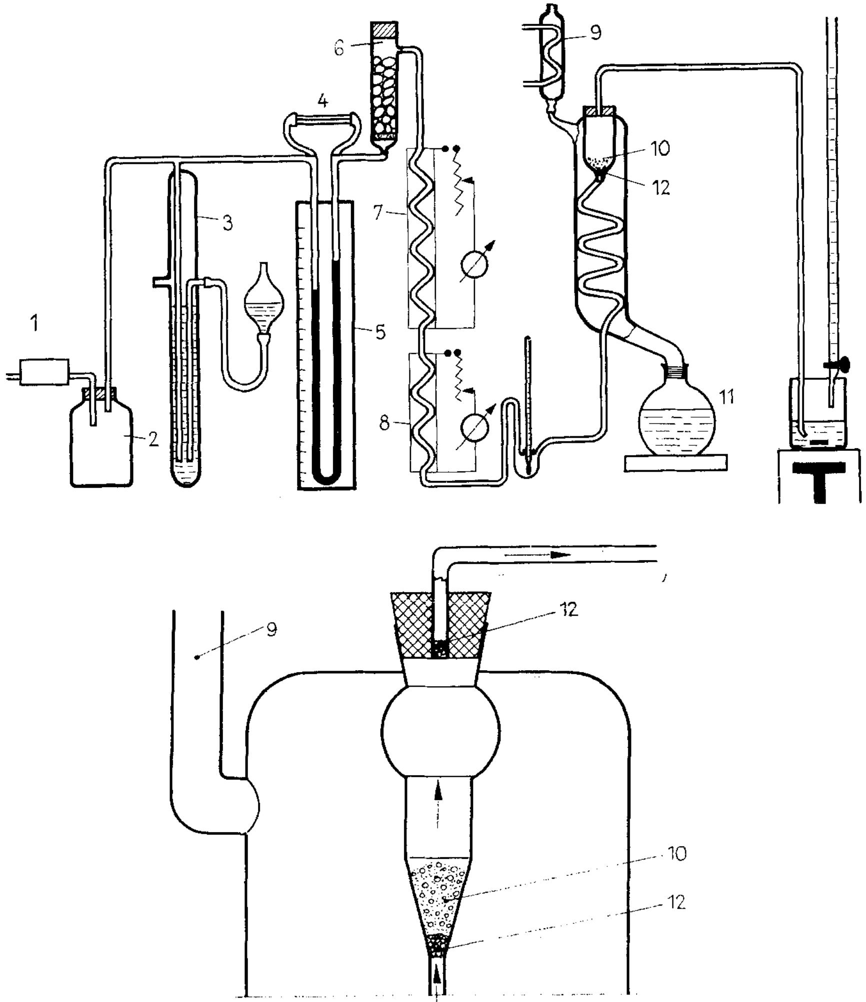

Fig. 1. 1. Compressor; 2. Pre-stabilizer; 3. Final stabilizer; 4. Capillary tube; 5. Pressurd gauge; 6. Vessel filled with $CaCl_2$; 7., 8. Pre-heaters; 9. Refrigerator; 10. Phial with fluidizee $(NH_4)_2HPO_4$; 11. Vessel with liquid; 12. Asbestos plug

of ammonium metavanadate. It was concluded that our results fit a kinetic model in which the nucleation is superficial and fast uninterrupted movement of the carrier gas takes place on the interfacial reactive surface, transmitted towards the particles at a constant rate. Mathematically the process is expressed by the following equation: $1-(1-\alpha)^{1/3} = kt$, where α is the transformation 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, taking into account the Arrhenius law $k = A_{\text{exp}}(-E/RT)$ the log k vs. $1/T$ plot was prepared, and from the slopes of the lines the activation energy was calculated. The experimental data obtained for various temperatures, particle sizes and carrier gases are given in Tables 1 and 2.

Table 1

Rate constants and activation energies for different particle sizes, using air as carrier gas

Temperature	Particle sizes		
	0.15–0.20 mm	0.25–0.30 mm	0.40–0.43 mm
°C	k(min^{-1})	k(min^{-1})	k(min^{-1})
98	$5.88 \cdot 10^{-3}$	$4.62 \cdot 10^{-3}$	$3.60 \cdot 10^{-3}$
108	$1.18 \cdot 10^{-2}$	$1.13 \cdot 10^{-2}$	$8.54 \cdot 10^{-3}$
113	$1.61 \cdot 10^{-2}$	$1.50 \cdot 10^{-2}$	$1.20 \cdot 10^{-2}$
E (kcal mole^{-1})	19.18 ± 0.86	22.19 ± 0.68	23.14 ± 0.76

Table 2

Rate constants and activation energies for different carrier gases, using 0.15—0.20 mm particle size

Temperature	Carrier gas		
	Air	Methane	Hydrogen
°C	k(min^{-1})	k(min^{-1})	k(min^{-1})
98	$5.88 \cdot 10^{-3}$	$6.84 \cdot 10^{-3}$	$8.98 \cdot 10^{-3}$
108	$1.17 \cdot 10^{-2}$	$1.58 \cdot 10^{-2}$	$2.18 \cdot 10^{-2}$
113	$1.61 \cdot 10^{-2}$	$2.16 \cdot 10^{-2}$	$3.19 \cdot 10^{-2}$
E (kcal mole^{-1})	19.18 ± 0.86	22.11 ± 0.68	24.82 ± 0.63

By using the least squares method, the confidence limits for the activation energy were calculated.

Conclusions

a) For the same particle size, at the same temperature, but for different carrier gases, the rate constant increases in the following order: air, methane, hydrogen. The activation energy increases in the same order. The increase is appreciable in the case of hydrogen due to its high diffusion rate.

b) For the same carrier gas (air), the rate constant increases with decreasing particle size. This is due to the defects whose number increases in the crumbling operation, and to the increases of the surface area.

c) This work shows that a fluidized bed may, under certain conditions, be used to arrive at kinetic data for clearly identified steps in thermal decompositions.

Of course the reaction studied is heterogeneous and the activation energy data obtained can be influenced by the crystal energies.

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RÉSUMÉ — On peut obtenir les paramètres thermodynamiques de la décomposition thermique de l'hydrogénophosphate di-ammonium par utilisation des lits fluidifiés. Avec les mêmes tailles de particles et la même température les valeurs des constants de vitesse et de l'énergie d'activation augmentent selon le gaz vecteur employé, en ordre air, méthane, hydrogène. En utilisant le même gaz vecteur (air), les constants de vitesse augmentent si la taille des particules diminue.

ZUSAMMENFASSUNG — Verläßliche thermodynamische Daten der thermischen Zersetzung von Diammoniumdiphosphat wurden durch Anwendung von fluidisierten Betten erhalten. Für gleiche Teilchengrößen bei gleichen Temperaturen und verschiedenen Trägergasen wachsen die Werte der Geschwindigkeitskonstanten und der Aktivierungsenergien in der Reihenfolge Luft, Methan, Wasserstoff. Bei gleichem Trägergas (Luft) nimmt die Geschwindigkeitskonstante mit abnehmender Größe zu.

Резюме — Получены надежные термоаналитические параметры для терморaспада $[NH_4]_2HPO_4$. В случае навески одинакового размера при одной и той же температуре, но при разных газах-носителях постоянная скорости и энергия активации увеличиваются в порядке: воздух, метан, водород. В случае одного и того же газа-носителя (воздух) постоянная скорости увеличивается, если размер навески уменьшается.