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Thermodynamic Studies of the Possibility of Free Carbon Formation during the Synthesis of Calcium Cyanamide by the Carbide-Free Method

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Abstract – The article presents the results of the study of the effect of the volumetric velocity of the initial gas mixture on the calcium cyanamide yield. In the studied range of volumetric velocity and CO_2: NH_3 ratio, the optimal temperature of calcium cyanamide synthesis was shown to be 800^0C. As a result of the research, the initial temperature of thermal decomposition of ammonia was calculated for the first time on the basis of new physicochemical constants by thermodynamic calculations and the probability of additional chemical reactions between ammonia and carbon dioxide was determined. The effect of the main technological parameters on the synthesis of calcium cyanamide was determined. The composition of the exhaust gases from calcium cyanamide synthesis reactors has been studied as a function of temperature.

Keywords – Thermodynamic, Free Carbon Formation, Synthesis, Calcium Cyanamide, Carbide-Free Method.

I. INTRODUCTION

The kinetic study of calcium cyanamide synthesis revealed the order of chemical reactions between ammonia and carbon dioxide, the limited phase of calcium cyanamide synthesis proved the diffusion of gaseous components through the product layer

Uzbekistan pays great attention to the development of the chemical industry, especially the production of mineral fertilizers. The food problem in the world is now sharply aggravated due to high population growth rates, a decrease in suitable arable land and fresh water supplies. In the production of high and high-quality crop yields, mineral fertilizers are of great importance.

In Uzbekistan, the main assortment of nitrogen fertilizers produced is ammonium nitrate, urea and ammonium sulfate, the use of which has led to acidification of millions of hectares of land for many years, which negatively affects the receipt of high yields of agricultural crops.

The chemical formula of calcium cyanamide $CaCN_2$, molecular weight equal to 80.11 carbon units, contains 34.98% of bound nitrogen in the amide form. Calcium cyanamide and ammonium nitrate are close in nitrogen

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content (35%), but it contains ammonia and nitrate forms of bound nitrogen, and its solubility in water is 2.5 g in 100 ml of water [2], i.e. almost 70 times less than the solubility of ammonium nitrate, which is important when saving the rate of application of mineral fertilizers, in particular, calcium cyanamide. In organic solvents and alcohol, calcium cyanamide is practically insoluble. Calcium cyanamide under normal conditions has a specific gravity of 2.3 g/m^3 and is a colorless rhombohedral or hexagonal crystal.

X-ray structural and IR spectroscopic methods of analysis have shown that the structural formula of calcium cyanamide has a symmetric structure.

Calcium cyanamide has a fairly high thermal stability, but at a temperature of 10900C and above, its sublimation begins, which at 1100-1500^{0}C is accompanied by partial decomposition. With an increase in temperature to 1346-1370^{0}C, calcium cyanamide begins to melt [30, p.68-76].

For a long time, calcium cyanamide was a raw material for the production of ammonia according to the reaction [3]:

$$CaCN_2+3H_2O(steam)=CaCO_3+2NH_3(gas)$$

This method of producing ammonia has lost its significance in connection with the beginning of its production through the chemical interaction of elemental hydrogen and nitrogen.

Calcium cyanamide interacts with water according to the following chemical reaction:

$$2CaCN_2+2H_2O=Ca(HCN_2)_2+CaOH_2$$

Mineral acids accelerate the process of hydrolysis of calcium cyanamide with the formation of free calcium cyanamide with a further possible transition to carbamide by reactions:

$$CaCN_2+2H_2O=Ca(OH)_2+H_2CN_2$$

$$H_2CN_2+H_2O=CO(NH_2)_2$$

At a temperature of 1100^{0}C or more, carbon monoxide decomposes calcium cyanamide by the reaction:

$$CaCN_2+CO=CaO+N_2+2C$$

In the temperature range 500-1100^{0}C, as a result of exposure to carbon dioxide, calcium cyanamide decomposes according to the reaction:

$$2CaCN_2+CO_2=2CaO+2N_2+3C$$

With an increase in temperature to 1400-1500^{0}C, calcium cyanamide can interact with carbon, as a result of which calcium cyanide is formed by the reaction:

$$CaCN_2+C=Ca(CN)_2$$

In the case of the simultaneous fusion of calcium cyanamide with sodium chloride and coal, it is possible to obtain sodium cyanide by the reaction:

$$CaCN_2+2NaCl+C=2NaCN+CaCl_2$$

When the ratio S: L = 1: 5, free cyanamide can be formed under the action of carbon dioxide:

$$CaCN_2+CO_2+H_2O=H_2CN_2+CaCO_3$$

Analysis of the above reactions shows that in experimental studies on the production of calcium cyanamide, special attention should be paid to excluding the action of water in a liquid or vapor state.

Practice shows that some compounds are used in the chemical industry, while others are used in agriculture. Although such compounds are rarely found, which are widely used both in agriculture and in the chemical industry. Calcium cyanamide, which, according to the above data, has universal physicochemical properties can also be ranked among such exceptional compounds.

Scientific research has established that the physiological calcium deficiency in soil salinity is one of the main factors limiting the salt tolerance of cotton and other crops. Therefore, the development of the production of mineral fertilizers based on our own raw materials, especially calcium-containing and alkaline species, such as calcium cyanamide and others, is important for growing crops in saline soils and limited water resources.

Calcium cyanamide is a slow-acting fertilizer and nitrogen from it is absorbed by plants more efficiently. When applied under fall plowing, it is preferable to other nitrogen fertilizers and has a sterilizing effect on harmful soil microflora.

The presence of free carbon or soot in calcium cyanamide has negative consequences. Such calcium cyanamide as a defoliant will contaminate raw cotton with soot, which will significantly complicate the processing of cotton fiber, the spread of soot in the environment and harmful effects on human health. In addition, the production of free cyanamide and other derivatives from calcium cyanamide will become more difficult, because it is necessary to additionally build a

filtration unit to remove soot from products, which, in turn, creates environmental problems.

Table 1. Heat effect, entropy and Gibbs energy change under standard conditions.

QP_{298}		S_{298}		GO_{298}	
cal/mol	J/mol	cal/mol·deg	J/mol·deg	cal/mol	J/mol
-40327	-168728,160	-7,765	-32,489	42640,97	178409.810

Table 2. Heat effect of reaction at different temperatures.

T1,K		873	973	1073
QPT1	cal/mol	-40292,335	-40274,638	-40247,533
	J/mol	-168583,120	-168509,080	-168395,670

1173	1273	1373	1473
-40204,606	-40139,005	-40043,603	39911,091
-168216,070	-167941,590	-167542,430	-166988,000

Table 3. Logarithm of the reaction equilibrium constant at different temperatures

T1,K	873	973	1073	1173	1273	1373	1473
106KPT1	-11,748	-10,703	-9,851	-9,143	-8,545	-8,032	-7.588

Due to the above factors, the study of the possibility of the formation of free carbon in the composition of calcium cyanamide is urgent.

In this regard, thermodynamic calculations were carried out for the possibility of free carbon formation when obtaining calcium cyanamide from lime, ammonia, and carbon dioxide. We made the assumption that the formation of free carbon can occur by the following chemical reaction:

$$2NH_3+CO_2=C+N_2+2H_2O+H_2+Q$$

When carrying out thermodynamic calculations, the ratio in the initial gas mixture was taken to be stoichiometric at a temperature of 873-1373K with a step of 100K.

Under standard conditions and constant pressure for the indicated reaction in accordance with Hess's law, the heat effects were calculated by the equation:

$$\Delta H^0_{298}=\sum\Delta H^0_{пр}-\sum\Delta H^0_{ис}$$

Where:

$-\sum\Delta H^0_{пр}$- the algebraic sum of the heats of products formed as a result of a chemical reaction under standard conditions, cal / mol;

$-\sum H^0_{ис}$- algebraic sum of the heats of formation of the starting components under standard conditions, count / mol.

It was established by thermodynamic calculations that ΔH^0_{298}=2257,2 cal / mol, and this proves the endothermicity of the studied chemical reaction under standard conditions.

It was also found that the change in the entropy of the reaction is equal to - 106.28 cal / mol · deg, i.e. this reaction is reversible.

The obtained value of the Gibbs energy change of 29413.19 cal/mol showed the thermodynamic probability of the reaction.

But the experimental studies carried out under standard conditions, given under standard conditions, contradicted this conclusion. Therefore, later it was decided to carry out thermodynamic calculations at high temperatures.

In this regard, using the Kirchhoff equation, the temperature dependence of the heat capacity was determined. Using this dependence, the thermodynamic parameters of the chemical reaction were calculated as a function of temperature (Table 4):

Table 4. Temperature dependence of thermodynamic parameters of a chemical reaction

T, K	873	973	1073	1173	1273	1373
ΔH_T^0, cal/mole	25406	25979	26240	26313	26675	26573
ΔG_T^0, cal/mole	25962	23598	20624	17100	13050	8477

The data obtained show that in the investigated temperature range 873-1373K, the thermal effects of the chemical reaction turned out to be endothermic. It should be noted that with an increase in temperature to 1173K, the thermal effects of the chemical reaction first decrease and then slightly decrease.

In subsequent thermodynamic calculations, the values of the Gibbs energy change were calculated, which showed that their absolute values decrease with increasing temperature.

This proves that the studied chemical reaction cannot proceed from a thermodynamic point of view, i.e. free carbon is not formed.

In the indicated temperature range, experiments were carried out on the synthesis of calcium cyanamide from carbon dioxide, ammonia and lime, as a result of which a white product was obtained, which also confirms the absence of free carbon.

Thus, thermodynamic calculations and experimentally proved that during the synthesis of calcium cyanamide from ammonia, carbon dioxide and calcium oxide in the temperature range 873-1373^{0}K, free carbon is not formed.

The chemical analysis of the products in previous studies showed the presence of mainly calcium cyanamide and a small amount of calcium oxide that did not enter into a chemical reaction. To confirm the results of chemical analysis, the samples were subjected to physicochemical analysis by the X-ray phase method, which in this case is an effective tool for determining the phase composition of products.

Samples of products synthesized at temperatures of 750, 800 and 900^0 C were subjected to X-ray phase analysis (Fig. 1-3). Other technological parameters for obtaining calcium cyanamide from lime, ammonia and carbon dioxide, such as the size of the initial charge granules, the composition of the granules, the ratio of carbon dioxide to ammonia , the volumetric velocity of the initial gas mixture and its passage time were the same for all product samples.

The X-ray diffraction pattern of the product obtained at 750^{0}C (Fig. 3) showed the presence of interplanar distances corresponding to calcium cyanamide (d = 4.88; 3.04; 2.99; 2.44; 2.19; 1.88 A^0) and unreacted calcium oxide (d = 2.31; 2.12; 1.94; 1.72 A^0). The intensity of the interplanar distances of calcium cyanamide is less than that of the samples obtained at 800^{0}C, and vice versa, the intensity of unreacted calcium oxide turned out to be higher, therefore, the temperature of 750^{0}C for obtaining calcium cyanamide is not optimal.

With an increase in the temperature of the process up to 800^{0}C (Fig. 1), the maximum intensity of interplanar distances of calcium cyanamide (d = 2.99; 2.46; 2.26; 2.08; 1.89; 1.85A^0) appears on the diffractogram and the minimum is for unreacted oxide calcium (d = 2.46; 1.61; 1.43A^0).

On the diffractogram of the sample obtained at 900^{0}C, the intensity of the interplanar distances of calcium cyanamide decreases (d = 2.99; 2.79; 1.85; 1.70A^0), and the unreacted calcium oxide increases (d = 2.41; 1.70 ; 1.45; 1.33A^0).

The results of chemical and X-ray phase analysis of the composition of the product at different temperatures can be explained by the mechanism of the process, where, in the initial period, the formation of calcium cyanamide, covering the entire surface of the granule, occurs at a high rate on the surface of the batch granules. Then the formation of calcium cyanamide occurs inside the granule as a result of diffusion of carbon dioxide and ammonia deep into the granule. At the same time, the CN_2^{2-} ion penetrates into the surface layer, where “vacancies” appear, i.e. free spaces for the formation of new cyanamide ions.

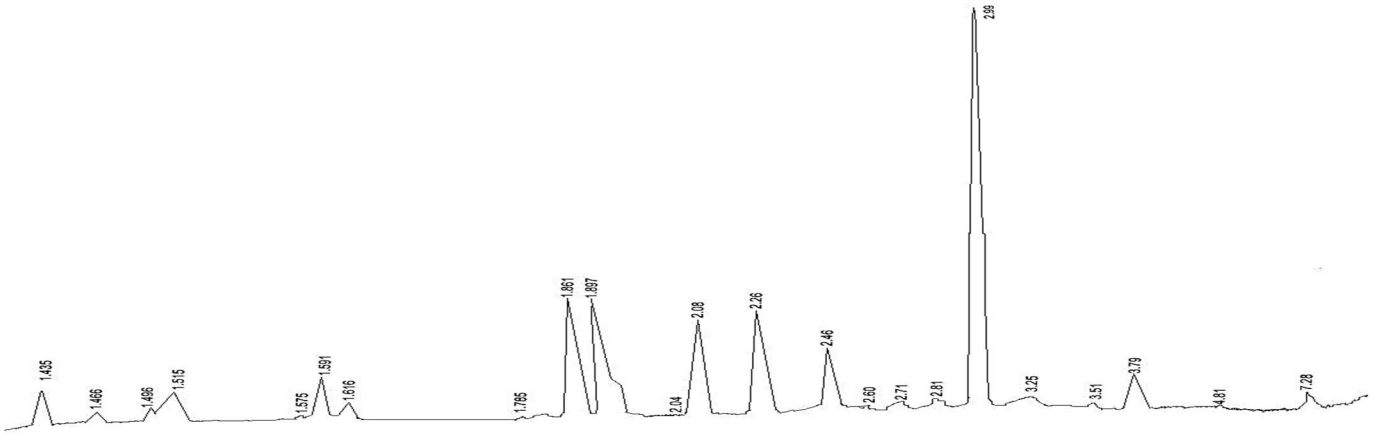

Figure: 1. X-ray diffraction pattern of a sample of calcium cyanamide obtained at 800^0C.

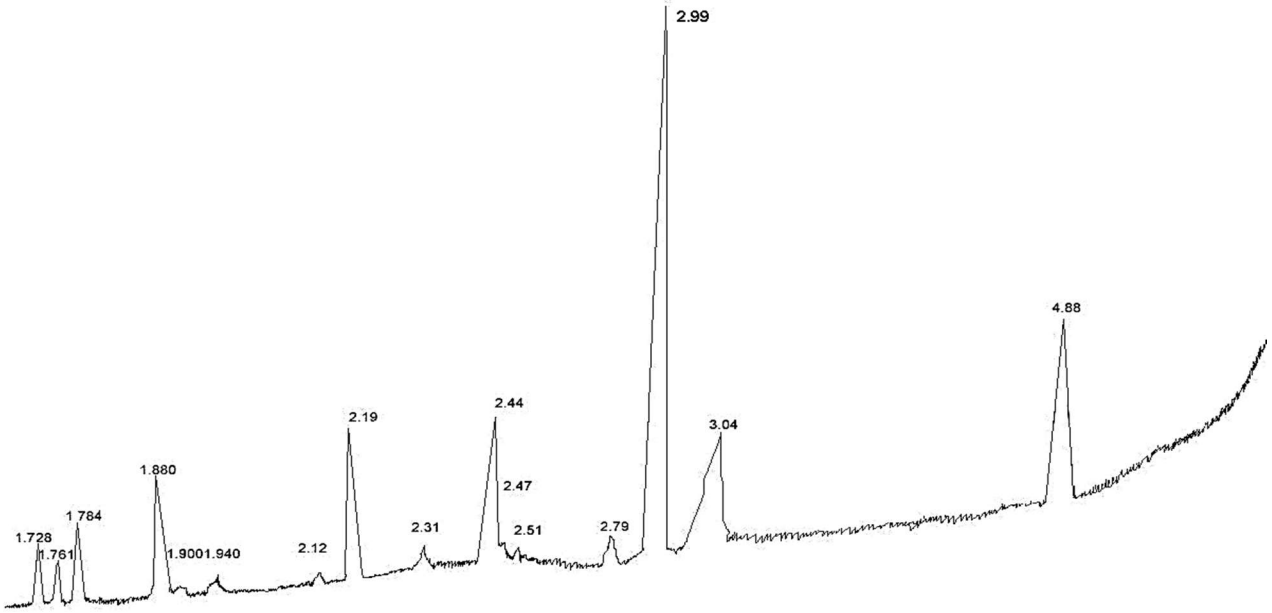

Figure: 2 X-ray diffraction pattern of a calcium cyanamide sample obtained with 7500C.

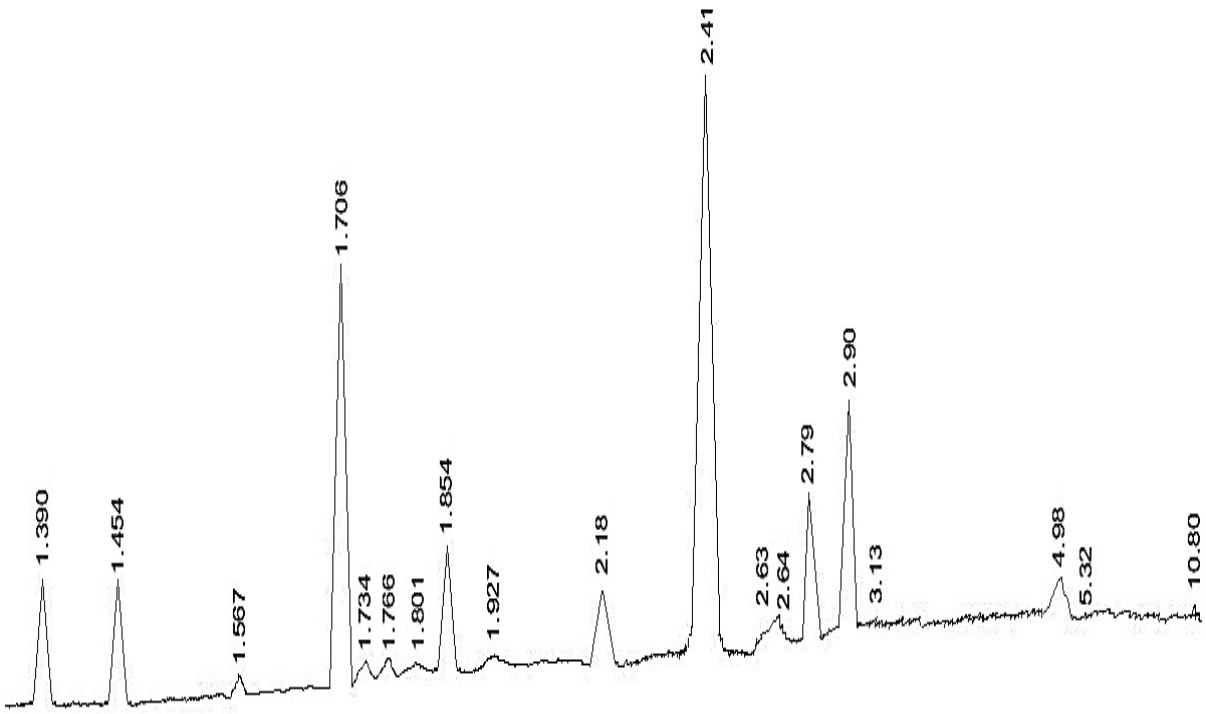

Figure: 3 X-ray diffraction pattern of a calcium cyanamide sample obtained with 9000C.

The foregoing allows us to confidently judge the probability of migration of calcium cyanamide ions deep into the granules, which occurs rather quickly and at temperatures below optimal. The rate of formation of active calcium oxide limits the overall rate of the process. An increase in temperature leads to an increase in the rate of formation of active calcium oxide, which also contributes to an increase in the total rate of the process. The amount of cyanamide ions formed corresponds to the rate of formation of active calcium oxide at the optimum temperature and the maximum yield of calcium cyanamide is achieved. An increase in the temperature of obtaining calcium cyanamide, which is more optimal, causes a decrease in the equilibrium yield of the product, and as a result, a smaller amount of calcium cyanamide ions enters the surface of the unreacted nucleus per unit time, which leads to a decrease in the total rate of the process.

The result of chemical and X-ray phase analysis confirms the optimal temperature of 800^0C for the synthesis of calcium cyanamide from lime, ammonia and carbon dioxide. The above mechanism of the process of synthesis of calcium cyanamide allows us to consider it sequentially conjugated, consisting in our case, of the process of formation of active calcium oxide and its interaction with a gas mixture of ammonia and carbon dioxide.

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