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Contributions to the Degenerated Branching Mechanism of the Thermal Decomposition of Ammonia[1]

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Abstract—By continuing our studies on the reaction kinetics and mechanism of ammonia thermal decomposition, new evidences are brought about supporting the indirectly branched chain mechanism advanced previously. The dependence of the induction period of the hydrogen formation as a reaction final product on the maximum concentration of hydrazine as the reaction molecular intermediate evidences indirectly branched chain mechanism affording preponderantly the hydrogen formation from hydrazine. The branching factor value of 0.00136 s^{-1} was found by means of three laws specific to the reaction developing according to three rules specific to the degenerated branching. This value indicates degenerated branching occurring rather as a scarce event according to literature data where this factor is shown to be between 0.00016 and 0.01666 s^{-1}.

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Since the mechanism of the ammonia thermal decomposition for hydrogen obtaining as a source of unpolluting fuel [1–3] is not entirely clear, we have considered this subject in our previous papers [4–11]. Thus, the kinetics of this reaction was studied at continuous flow conditions in quartz reactors over the 600–900°C temperature range and ammonia flow rates from 200 to 100 cm^3/min. The concentrations of ammonia, hydrogen and nitrogen as final decomposition products were measured by pH-metric titration and gas-chromatographically [4, 8, 10].

The kinetic parameters n, k, E_a, and A have been estimated [4, 10]. The analysts of the kinetic parameters afforded the conclusion that the ammonia thermal decomposition is not a simple reaction, but it develops as a homogeneous-heterogeneous chain and the overall reaction energy is smaller than the initiation reaction energy. The induction periods in the formation of the reaction products were found to appear on the kinetic curves [5, 10, 12–14].

The kinetic modeling of the reaction under study in dynamic conditions consisted of the building of an extended mechanistic model including also heterogeneous processes suggested by previous studies [1, 2] describing the temporal evolution noticed experimentally [6]. The insignificant reactions were identified by sensitivity analyses [15–18] on the basis of the normalized sensitivity coefficients and removed from the model. The reduced mechanism (involving 21 elementary reactions in comparison with 55 stages in the extended model) was confirmed by the coincidence of the kinetic curves for the reagent and reaction products obtained by numerical integration with those obtained on the basis of the extended model.

In Table 1 the reduced mechanism for the reaction of ammonia decomposition at 800°C is presented. The extended mechanism was presented and discussed in detail earlier [19].

It is worth noting the coincidence of the kinetic curves obtained by numerical integration based on extended mechanism (solid lines) with the kinetic curves based on reduced mechanism (symbols) in Fig. 1. The good agreement between the kinetic curves based on the extended and reduced mechanisms justifies the elimination of unimportant reactions from the theoretical model.

Moreover, a good agreement between the time evolution of the NH_3, N_2 and H_2 concentrations calculated on the basis of the reduced mechanism and the corresponding experimental kinetic curves (Fig. 2) is quite remarkable.

Numerical integration, fitting of kinetic models with experimental data and sensitivity analysis were made using KINTECUS software [20].

The investigation of introduced heterogeneous reactions led to the conclusion that the relatively stable molecular intermediate N_2H_4 is accumulated during the initial reaction period (short contact times). This may explain the induction period and the delay in the appearance of the final products confirming the

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Table 1. The mechanism of thermal decomposition of NH_3 (reduced model)

No.	Reaction	A, l mol^{-1} s^{-1}	m	E_a, kJ/mol
1	$NH_3 + M[NH_3; N_2; H_2] = NH_2 + H + M$	2.20×10^{13}	0	391.34
2	$NH_3 + NH = 2NH_2$	3.16×10^{11}	0	112.08
3	$NH_2 + NH = NH_3 + N$	1.00×10^{10}	0	8.37
4	$NH_3 + NH_2 = N_2H_3 + H_2$	1.00×10^{8}	0.5	90.43
5	$NH + H_2 = NH_2 + H$	1.00×10^{11}	0	84.03
6	$NH + H = N + H_2$	3.20×10^{10}	0	1.36
7	$N_2H_3 + M[N_2;NH_3;N_2H_4] = NH_2 + NH + M$	5.00×10^{13}	0	251.21
8	$N_2H_3 + M[N_2;NH_3;N_2H_4] = N_2H_2 + H + M$	1.00×10^{14}	0	138.16
9	$N_2H_2 + M[N_2;H_2] = NNH + H + M$	5.00×10^{13}	0	209.34
10	$NNH + M[N_2;H_2] = N_2 + H + M$	1.00×10^{10}	0.5	12.81
11	$N_2H_2 + NH_2 = NH_3 + NNH$	8.80×10^{-5}	4.05	−6.75
12	$N_2H_2 + H = NNH + H_2$	85	2.63	−0.963
13	$2NH_2 + $ act. site{s} $= N_2H_4 +$ act. site{s}	$k = 4.23 \times 10^{13}$ l mol^{-1} s^{-1}		
14	$N_2H_4 + M[N_2;NH_3;N_2H_4] = 2NH_2 + M$	5.00×10^{11}	0	251.21
15	$N_2H_4 + M[N_2;NH_3;N_2H_4] = N_2H_3 + H + M$	1.00×10^{12}	0	266.28
16	$N_2H_4 + NH = NH_2 + N_2H_3$	1.00×10^{6}	1.5	8.37
17	$N_2H_4 + H = N_2H_3 + H_2$	7.00×10^{9}	0	10.47
18	$N_2H_4 + N = N_2H_3 + NH$	1.00×10^{7}	1	8.37
19	$N_2H_4 + NH_2 = N_2H_3 + NH_3$	1.80×10^{3}	1.71	−5.78
20	$NH_3 + H = NH_2 + H_2$	5.42×10^{2}	2.4	41.53
21	$2H +$ act. site{s} $= H_2 +$ act. site{s}	$k = 3.51 \times 10^{14}$ l mol^{-1} s^{-1}		

Note. $k = AT^m\exp(-E_a/RT)$, m—temperature exponent in Kassel equation.

degenerated branching mechanism advanced for the reaction of ammonia thermal decomposition in a quartz reactor in agreement with the general kinetic theory of the indirectly branched chain reactions [12, 13].

The experimental identification of N_2H_4 as a molecular reaction intermediate was confirmed by the theoretical curves of its time evolution under suggestion that the hydrogen is mainly formed from N_2H_4 [9].

Important evidences supporting the degenerated branching mechanism brought in the present paper for the ammonia thermal decomposition consist in the experimental finding that the induction period of the H_2 formation coincides with the N_2H_4 maximum concentration on the theoretical kinetic curve. This coincidence affords the conclusion that hydrogen is formed preponderantly from hydrazine as the main unstable molecular intermediate, leading to the degenerated branching [9, 10, 12, 13].

The branching factor, φ, referred also as overall branching factor [12, 13] represents the difference between the frequencies of the branched propagation and interruption reactions. Since the formation of an unstable molecular intermediate is a necessary condition for the degenerated branching, and this intermediate could give branching only after being accumulated in a certain critical concentration in the main reaction chain [12, 13, 21], the degenerated branching would occur much slower than the direct branching [12, 13]. For example, we have to mention that $\varphi = 80$ s^{-1} for hydrogen burning (direct branching) while for methane oxidation (degenerated branching), φ can lie between 0.00016 and 0.01666 s^{-1} [21, 22].

The branching factor in the reaction of ammonia thermal decomposition was estimated on the basis of experimental data by means of three kinetic laws specific to the degenerated branching reactions resulting from the Semenov law [12, 13]. The φ value of 0.00136 s^{-1} was calculated within the experimental errors which falls in the interval characteristic of degenerated branching reactions. This fact strongly supports the degenerated branching mechanism of the ammonia thermal decomposition [21–24].

EXPERIMENTAL

In order to study the induction period for the H_2 and N_2 formation as the final products of ammonia thermal decomposition at 700, 750 and 800°C, as well

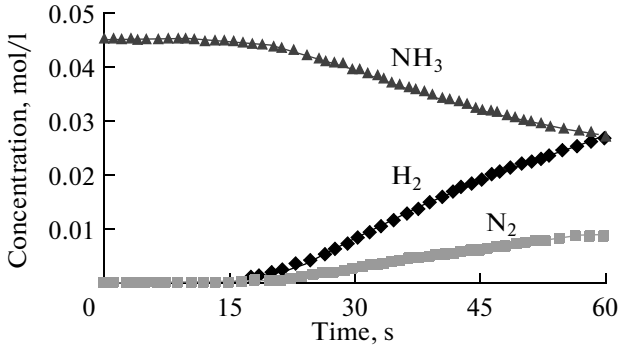

Fig. 1. Comparison of the theoretical kinetic curves obtained by numerical integration based on the extended mechanism (solid lines) and on the reduced mechanism (symbols).

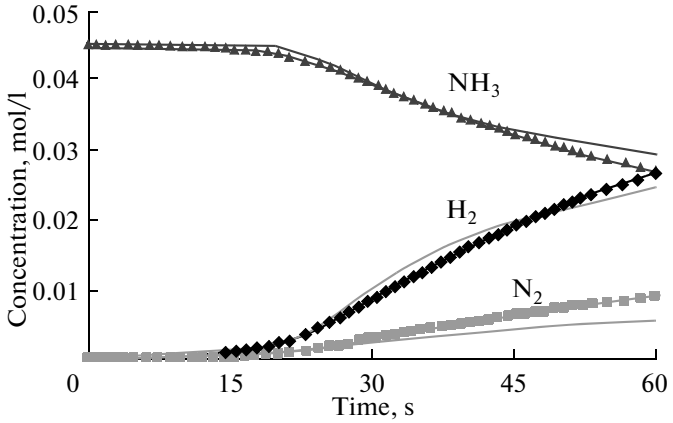

Fig. 2. Kinetic curves of NH_3 consumption and N_2 and H_2 formation (theoretical reduced model—symbols, experimental data—solid lines).

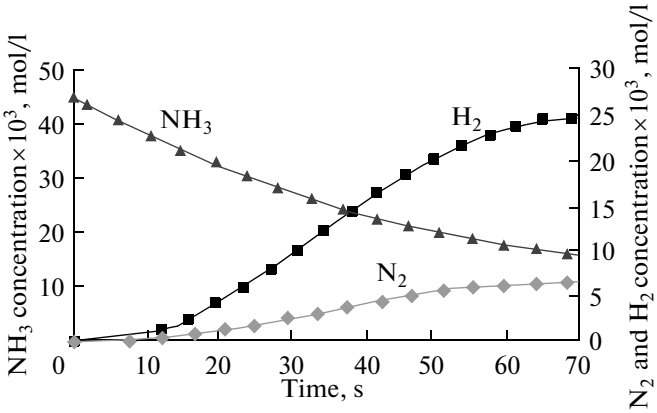

Fig. 3. Kinetic curves of NH_3 consumption and hydrogen and nitrogen formation at 800°C.

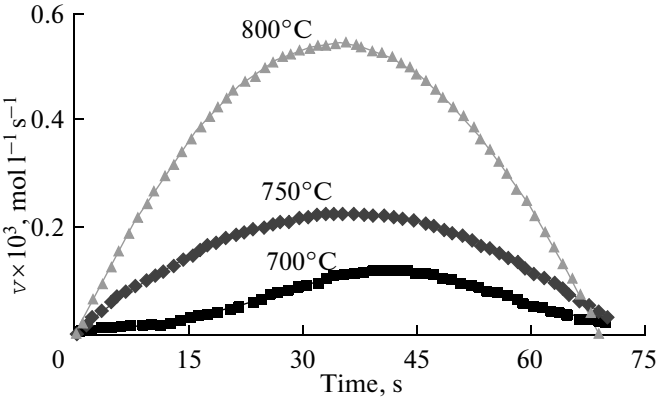

Fig. 4. Rate of H_2 formation versus contact time at 700, 750 and 800°C.

as for estimating the branching factor at 800°C, the experimental data obtained in previous works [4–6, 8–10] for the reaction kinetics were used.

The experiments were carried out at continuous flow conditions using the following components: a quartz reactor (volume 348.813 cm^3, surface to volume ratio $S/V = 0.85\ cm^{-1}$), an electric oven with a chromel-alumel thermocouple, a "Wisog 1100 Zurrich" flowmeter for ammonia, a cylinder with 99.98% NH_3, a pressure reducer, a drying vessel, a SRT-46 thermo-regulator and a rheostat affording the temperature regulation within the 600–900°C range and a flow rate of 200–1000 cm^3/min.

The ammonia and final reaction products were analyzed by pH-metric titration and gas-chromatographically and the hydrazine was determined by a specific spectrophotometrical method [25].

RESULTS AND DISCUSSION

Study of Induction Period

In Fig. 3 the kinetic curves are depicted for the ammonia consumption and hydrogen and nitrogen formation at 800°C under dynamic conditions [4, 5, 10].

Starting from the definition of the induction period [13a] as the time required for the rate of the final product formation to attain the maximum value, the rates of H_2 and N_2 formation versus contact time for 700, 750 and 800°C are plotted in Figs. 4 and 5.

Table 2 presents the induction periods of H_2 and N_2 formation by ammonia thermal decomposition at the above mentioned three temperatures.

The induction periods of both H_2 and N_2 formations decreased with increasing temperature. The induction periods for N_2 are longer than those for H_2

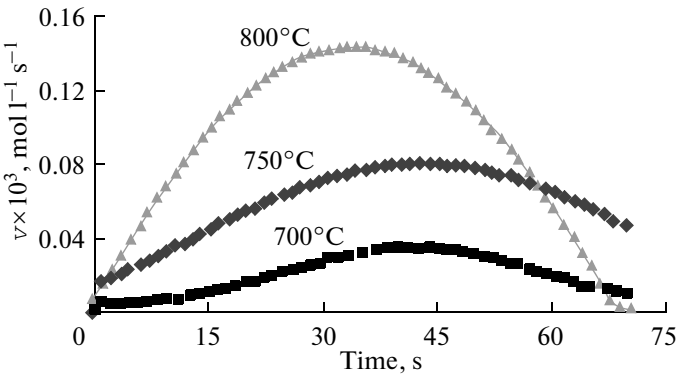

Fig. 5. Rate of N_2 formation versus contact time at 700, 750 and 800°C.

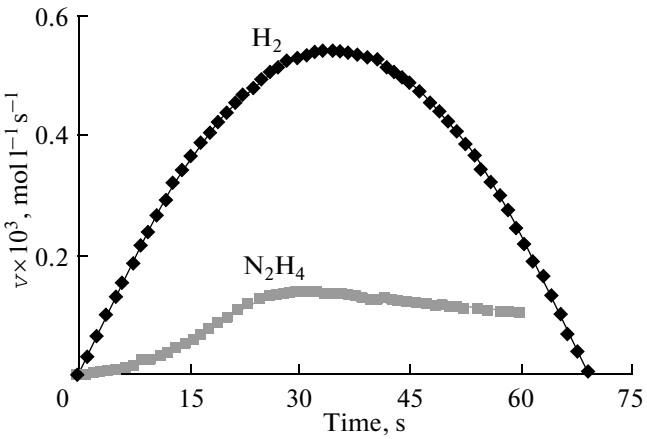

Fig. 6. Rates of N_2H_4 and H_2 formation versus contact time at 800°C.

at the three temperatures indicating that the nitrogen is formed after the hydrogen formation.

An essential finding supporting the degenerated branching mechanism of the ammonia thermal decomposition consists in the fact that the contact time corresponding to the N_2H_4 maximum concentration [6, 9, 26–35] on the theoretical kinetic curve (30 s) coincides with induction period of H_2 formation at 800°C (32 s) within the experimental error, thus indicating the hydrogen preponderant formation from hydrazine as the molecular unstable intermediate responsible for the degenerated branching (Fig. 6).

Upon filling the reactor with 30 g of quartz pieces, the induction period for the H_2 formation at 800°C reduces to 30 s, i.e., it becomes shorter than that for the empty reactor [36].

According to these findings supporting the degenerated branching reaction mechanism previously advanced by us, the reaction of ammonia thermal decomposition could be directed to a certain objective as follows:

(1) if the H_2 production at a maximum rate at the reaction onset is desirable, the maximum concentration of N_2H_4 can be admitted just at the beginning of the reaction, the induction period being thus entirely canceled;

(2) for the production of N_2H_4 at a higher rate, the contact area for the major radical, $^{\bullet}NH_2$, can be increased by filling the reactor with quartz pieces. This results in a higher S/V ratio in the reactor and consequently in a higher N_2H_4 concentration.

Estimation of the Branching Factor

According to the general theory of the branched chain reactions the reaction rate expressed by means of the reaction product depends inversely proportional on the life time of the active center originating the branching. Since with degenerated branching reactions this active center is the intermediate compound D (N_2H_4 for the reaction under study), having a much longer life time than the radicals and being able to generate new radicals, the reaction would develop similarly to the directly branched chain reactions although much slower.

Based on this theory, the kinetic law expressing the rate of the intermediate compound D formation is given by the relationship [13b]:

$$\frac{d[D]}{dt} = v_i\upsilon + [f(\upsilon\eta_m - 1) - g - \varphi_d][D], \qquad (1)$$

where v_i—rate of radical initiation, υ—length of the simple chain, f—rate factor for branching from D, t—contact time, η_m—chain multiplication factor, g and φ_d—rate factors for homogeneous and heterogeneous consumption of D, respectively. In Eq. (1),

$$\varphi = (\upsilon\eta_m - 1)f - g - \varphi_d \qquad (2)$$

referred to as overall branching factor, is given by the frequency difference between the branched propagation and interruption of reactions.

Table 2. Induction periods of H_2 and N_2 formation at 700, 750 and 800°C

T, °C	Induction period, s	
	H_2	N_2
700	42	43
750	36	41
800	32	34

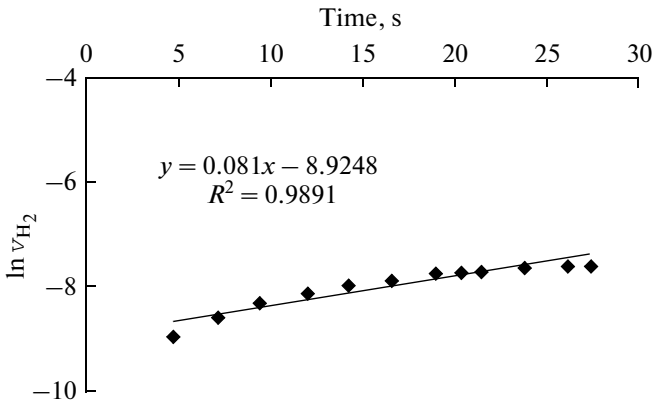

Fig. 7. Plot of $\ln v_{H_2}$ versus contact time at 800°C according Eq. (10).

By denoting the concentration of the intermediate D as n, Eq. (1) takes the form:

$$\frac{dn}{dt} = v_i\upsilon + \varphi n. \quad (3)$$

For $\varphi > 0$ and the initial conditions $\begin{cases} t = 0 \\ n = 0 \end{cases}$, the integration of Eq. (3) leads to the following equations describing the intermediate compound concentration (n) and the formation rate of the reaction product (H_2):

$$n = \frac{v_i\upsilon}{\varphi}\left(e^{\varphi t} - 1\right) \approx \frac{v_i\upsilon}{\varphi}e^{\varphi t}, \quad (4)$$

Table 3. The dependence between the rate of H_2 formation and the contact time

t, s	$[H_2] \times 10^3$, mol/l	$v_{H_2} \times 10^3$, mol l^{-1} s^{-1}	$\ln v_{H_2}$ [mol l^{-1} s^{-1}]
0	0	0	–
2.37	0.0080	0.0358	−10.2300
4.74	0.3590	0.1128	−8.9602
7.11	0.9611	0.1876	−8.5809
9.49	1.6067	0.2326	−8.3213
11.86	2.2990	0.2949	−8.1287
14.23	3.0409	0.3423	−7.9796
16.61	3.8354	0.3853	−7.8614
18.98	4.6852	0.4234	−7.7670
21.35	5.5928	0.4566	−7.7271
23.72	6.5599	0.5176	−7.6915
27.28	8.1245	0.6266	−7.6320

respectively

$$v_{H_2} = \frac{v_i\upsilon}{\varphi\Delta\tau}\left(e^{\varphi t} - 1\right) \approx \frac{v_i\upsilon}{\varphi\Delta\tau}e^{\varphi t}, \quad (5)$$

where $\Delta\tau$ stands for the life time of the molecular intermediate, D [12].

According to these rules representing the Semenov laws for the degenerated branching reactions [12, 13], for $\varphi > 0$, the D concentration increases exponentially in time at a constant temperature as well as the formation rate of the final product coming from D as can be seen on the experimental kinetic curves.

For the rate of the final reaction products formation, Eq. (5) can be rewritten as

$$v_{H_2} = \frac{d[H_2]}{dt} = \frac{v_i\upsilon}{\varphi\Delta\tau}e^{\varphi t}. \quad (6)$$

By separating the variables and integrating with the initial conditions $\begin{cases} t = 0 \\ [H_2] = 0 \end{cases}$ one obtains:

$$[H_2] = \frac{v_i\upsilon}{\varphi^2\Delta\tau}\left(e^{\varphi t} - 1\right); \quad [H_2] \approx \frac{v_i\upsilon}{\varphi^2\Delta\tau}e^{\varphi t}. \quad (7)$$

By taking Eq. (6) into account, Eq. (7) becomes:

$$[H_2] = \frac{v_{H_2}}{\varphi} \quad \text{or} \quad v_{H_2} = \varphi[H_2]. \quad (8)$$

Using relationships (4), (6) and (8), one can estimate the branching factor of the reaction from experimental data which agrees with the advanced mechanism based on the Semenov's theory of degenerated branching reactions.

Linearization of Eqs. (4) and (6) for the reaction under study leads to Eqs. (9) and (10):

$$\ln n = \ln\frac{v_i\upsilon}{\varphi} + \varphi t \quad \left(n = [N_2H_4]\right), \quad (9)$$

$$\ln v_{H_2} = \ln\frac{v_i\upsilon}{\varphi\Delta\tau} + \varphi t. \quad (10)$$

The φ values can be estimated from the plots of $\ln[N_2H_4]$ versus t and $\ln v_{H_2}$ versus t.

From Eqs. (8) and (10) along with the data of Table 3, the branching factors φ equal to 0.00144 and 0.00135 s^{-1}, respectively, are obtained. As an example, the graphical representation of Eq. (10) is illustrated in Fig. 7. The φ value of 0.00144 s^{-1} is obtained from Fig. 8, where Eq. (9) is plotted on the basis of data of Table 4.

The values obtained by means of three theoretical relations based on the Semenov's theory for the degenerated branching reactions using the experimental data are in good agreement. The average value of $\varphi = 0.001383$ s^{-1} at 800°C lies within the variation range for this type of chain mechanism [21].

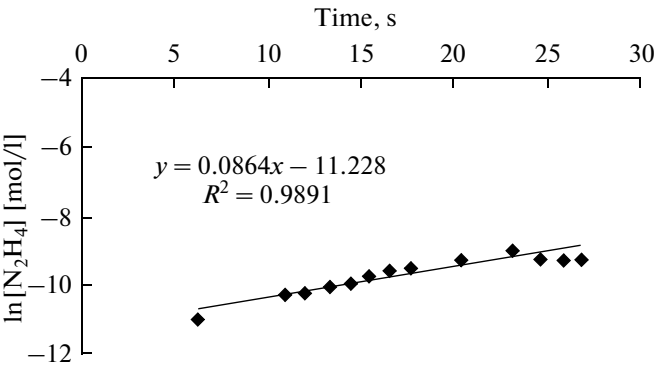

Fig. 8. Plot of $\ln v_{N_2H_2}$ versus contact time at 800°C according Eq. (9).

(1) The induction periods of N_2 formation at three temperatures (700, 750 and 800°C) are longer than those of H_2 suggesting that N_2 is produced thereupon the H_2 formation.

(2) The agreement between the induction period of H_2 formation and the contact time for the maximum N_2H_4 concentration supports the preponderant formation of H_2 from N_2H_4 and also the degenerated branching homogeneous-heterogeneous mechanism.

(3) Based on the experimental data and Semenov's theoretical rules specific to the degenerated branching reactions, the branching factor was estimated in three ways and a good agreement was found. According to the theory of the degenerated branching reactions, the branching factor of 0.00136 s^{-1} implies that the branching is a scarce event, where φ can take values between 0.00016 and 0.016666 s^{-1}.

Table 4. The dependence between the concentration of N_2H_4 and the contact time *t*

t, s	$[N_2H_4]$, mol/l	$\ln[N_2H_4]$ [mol/l]
6	1.13×10^{-5}	−11.009
11	2.93×10^{-5}	−10.2938
12	3.50×10^{-5}	−10.2602
13	4.33×10^{-5}	−10.0474
14.5	5.00×10^{-5}	−9.9034
15.5	5.74×10^{-5}	−9.7654
16.6	6.60×10^{-5}	−9.6258
17.7	7.51×10^{-5}	−9.4966
20.3	9.68×10^{-5}	−9.2528
23.1	1.18×10^{-4}	−9.0348
24.6	1.27×10^{-4}	−9.1981
25.8	1.32×10^{-4}	−9.1992
26.8	1.35×10^{-4}	−9.2199

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