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A NEW MODEL OF GAS–SOLID KINETICS: THE CASE OF AMMONIUM CARBAMATE FORMATION AND DECOMPOSITION

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ABSTRACT

The kinetics of the two opposite reactions

$$CO_{2(g)} + 2NH_{3(g)} \underset{2}{\overset{1}{\rightleftarrows}} NH_2\text{-}CO_2\text{-}NH_{4(s)}$$

have been followed manometrically. The initial orders of reaction 1 are 1 with respect to each reactant, which can be interpreted by assuming the transitory formation of carbamic acid. During the course of the reaction with a stoichiometric mixture at a total pressure P, the net rate is expressed by $r_{net} = k(P - P_{eq})^2$. This expression is explained by a mechanism of crystal growth (and decrease). The factor k depends primarily on the surface state and area.

LIST OF SYMBOLS

A	carbon dioxide
B	ammonia
c	concentration
C	ammonium carbamate
D	carbamic acid
E	activation energy
H	enthalpy
k	rate constant
K	equilibrium constant
m	overall order
n	mole number
P	pressure
r	reaction rate
R	ideal gas constant
S	area
T	temperature
t	time

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Greek letters

α	partial order with respect to A
β	partial order with respect to B
Δ	variation
ϵ	partial order with respect to any component
ν	algebraic stoichiometric coefficient

Subscripts

eq	in equilibrium conditions
g	in the gaseous state
i	relative to component i
s	in the solid state

Superscripts

0	in initial conditions

INTRODUCTION

The equilibrium of formation and decomposition of ammonium carbamate has been the subject of numerous studies [1–6]

$$\underset{\text{(A)}}{CO_{2(g)}} + \underset{\text{(B)}}{2NH_{3(g)}} \underset{2}{\overset{1}{\rightleftarrows}} \underset{\text{(C)}}{NH_2\text{–}CO_2\text{–}NH_{4(s)}}$$

It has been studied in our laboratory because of its applicability to the energy generation (exothermal reaction (1)) and storage (endothermal reaction (2)) [7]. The equilibrium constants K_p relative to partial pressures and total equilibrium pressures P_{eq} for stoichiometric gaseous mixtures are relatively well known. Figure 1 shows the curve P_{eq} vs. T for operating temperatures in our work, which are less than 60 °C (i.e. $P_{eq} < 1$ atm), since at higher temperatures the dehydration of ammonium carbamate to urea complicates the system [8].

The kinetics of reactions (1) and (2) are little known, and the literature data are conflicting. The first are reported by Naumann [1], but follow no kinetic law. More recent results on the decomposition reaction [2] have been given by Janjic [6] in the form of curves P vs. t, but, again, without any mathematical law. Laurent and Kikindai [9] attempted to justify the partial orders that they postulate a priori: 1 with respect to CO_2, 2 with respect to NH_3 and 0 with respect to carbamate. This hypothesis is valid only for the so-called "simple" reactions [10], and there is no a priori reason why this

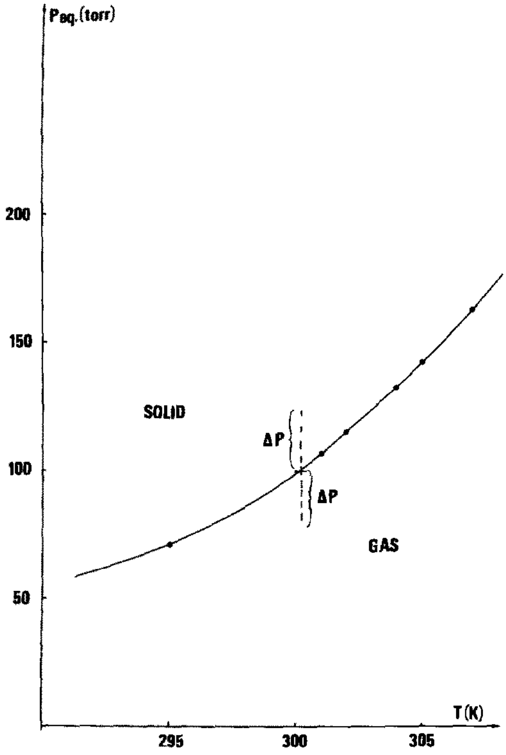

Fig. 1. Equilibrium pressure of ammonium carbamate as a function of temperature.

should be the case in reactions (1) and (2). Moreover, these workers find a negative activation energy for reaction (1). Paradoxically, the same result is claimed by Lishnevskii and Madzievskaya [11] for the initial rate of reaction (1), measured between 0 and −78 °C. This can be accounted for, besides assuming a termolecular reaction, by assuming in the customary way [10] that reaction (1) results from two component steps

$$A + B \rightleftarrows D \tag{1a}$$

$$D + B \rightarrow C \tag{1b}$$

D being in the present case carbamic acid, which has not yet been isolated, but the transitory existence of which can be postulated. Hence $r_1 = k_1(\mathrm{A})(\mathrm{B})^2$ with $k_1 = k_{1b}K_{1a}$ and, therefore $E_1 = E_{1b} + \Delta H_{1a}$. It can be observed that $E_1 < 0$ if, in the operating temperature interval $E_{1b} < -\Delta H_{1a}$.

Finally, the only kinetic equation to be found in the literature is that of Frejacques [12] which, rewritten with our notations, reads

$$r = kS\left(P^2 - P_{\mathrm{eq}}^2\right) \tag{1}$$

with

$$\log_{10}k = \log_{10}k_0 - \frac{530}{T} \tag{2}$$

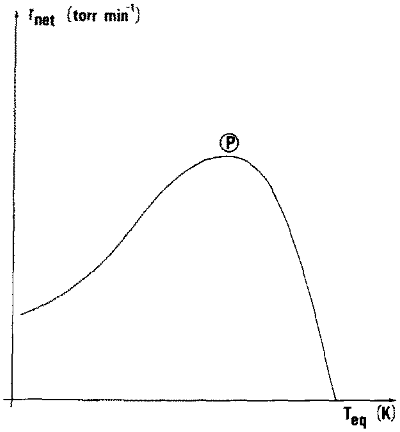

Fig. 2. Isobaric representation of r_{net} vs. T.

Expression (1) is that of a net reaction rate, which becomes nil when $P = P_{\text{eq}}$. The isobar graph is therefore that of Fig. 2. Unfortunately, no experimental data are given for substantiation of eqn. (1). We therefore attempted to re-examine the kinetics of reactions (1) and (2), reporting both our experimental data and the resulting equations. We kept in mind the following propositions [10]:

(1) The system is heterogeneous, and reaction (2) is a priori also heterogeneous. It is not obvious that reaction (1) is homogeneous, in spite of the fact that both reactants are gases. If, as has been reported [11], reactor walls play an accelerating role in this reaction, then it is kinetically heterogeneous.

(2) The net rate

$$r_{\text{net}} = r_1 - r_2 \tag{3}$$

has to be carefully distinguished from the individual rates of the component reactions. This net rate is compulsorily equal to zero when equilibrium is reached. The rates r_1 and r_2 can be measured in initial conditions (for each of them).

(3) Putting rates in the monomial form

$$r = k\prod_i P_i^{\epsilon_i} \tag{4}$$

is traditional, but not necessarily justified (at any rate for reaction 2). Obtaining a large overall order (e.g. larger than 3) suggests in classical kinetics that a slowing down of the reaction is occurring, for instance due to the inhibiting influence of a product.

(4) The well known ambiguity of formal kinetics can be removed only if the different parameters that it involves are measured as accurately as possible.

EXPERIMENTAL

Apparatus

The apparatus used is basically a batch reactor made of Pyrex® glass. The gases CO_2 and NH_3 are fed from desiccant columns, packed respectively with P_2O_5 and soda lime where they are allowed to stay for more than 12 h, water playing an accelerating role in carbamate formation [13]. Their total pressure is followed with a mercury manometer as a function of time. As the temperature was always close to ambient, no attempt was made to fit the apparatus with a special regulating assembly. The room in which it is installed is at a fixed temperature. The decomposition was studied immediately after carbamate formation, on the actual sample formed. The rate in this batch reactor would normally be expressed as $(1/\nu_i)(\mathrm{d}n_i/\mathrm{d}t)$ [10]. For the sake of simplicity, we shall consider in the sequel $(\mathrm{d}P_i/\mathrm{d}t)$. For a gaseous component, the relationship between both derivatives is

$$\frac{\mathrm{d}P_i}{\mathrm{d}t} = \left(\frac{RT}{V}\right)\left(\frac{\mathrm{d}n_i}{\mathrm{d}t}\right)$$

V being the constant volume of the reactor, equal to 291 cm^3, so that

$$\frac{\mathrm{d}n_i}{\mathrm{d}t}(\text{mole/unit time}) = \left(\frac{4.7\times10^{-3}}{T}\right)\left(\frac{\mathrm{d}P_i}{\mathrm{d}t}\right)(\text{torr/unit time})$$

RESULTS

Figure 3 gives an example of the curves obtained for the formation (1) and for the decomposition (2) of carbamate at the same temperature (307 K). The common asymptote at $P_{\mathrm{eq}} = 163$ torr is clearly manifested, although it is reached only after a very long time. The conventional exploitation of curve (1) consists in representing $\ln(-\mathrm{d}P/\mathrm{d}t)$ as a function of $\ln P$. Figure 4 shows that a straight line is obtained, but with a value of the slope (i.e. an overall order) larger than 4, which is of dubious interpretation in classical kinetics according to proposition (3) above. The reason for such a high apparent order is obviously the occurrence of the reverse reaction (2) from the very start. Therefore, an exploitation through the expression of a net rate is certainly more convenient and we addressed ourselves to the formula of Frejacques (1), which, in its integrated form, reads

$$\ln\left(\frac{P+P_{\mathrm{eq}}}{P-P_{\mathrm{eq}}}\right) = 2P_{\mathrm{eq}}kt + \ln\left(\frac{P^0+P_{\mathrm{eq}}}{P^0-P_{\mathrm{eq}}}\right) \qquad (5)$$

for formation and if the same net rate expression is supposed to hold for

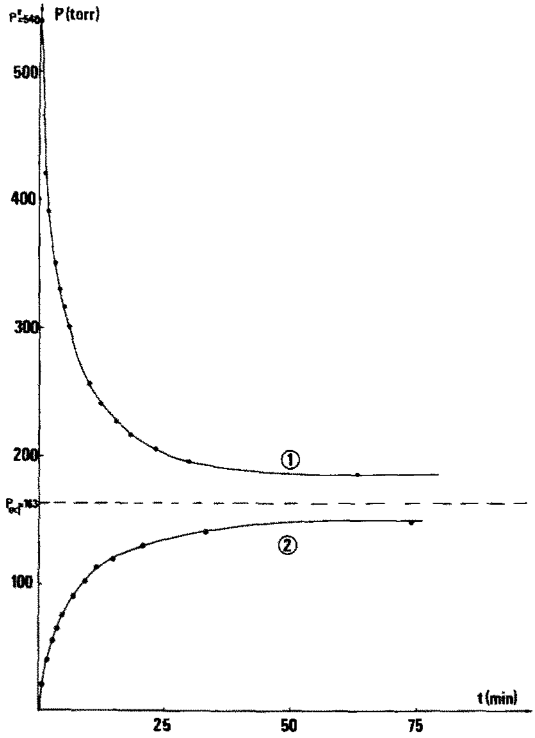

Fig. 3. Kinetics of opposite reactions at $T = 307$ K. (1), Formation (initial mixture: stoichiometric); (2), decomposition.

decomposition

$$\ln \frac{P_{\mathrm{eq}} + P}{P_{\mathrm{eq}} - P} = 2P_{\mathrm{eq}}kt \tag{6}$$

Figure 5 shows that neither formula is obeyed by our results.

If, on the other hand, we compare these results to those of Janjic [6] at very close temperatures there is a significant difference. However, Janjic's results are also not amenable to the formula of Frejacques. Finally, we applied to our results the kinetics postulated by Laurent and Kikindai [9], i.e.

$$-\frac{\mathrm{d}P}{\mathrm{d}t} = k_1 P^3 - k_2$$

but could not linearize our points (Fig. 6). Our data therefore do not accord with kinetic results already reported and we attempted to formulate an alternative explanation.

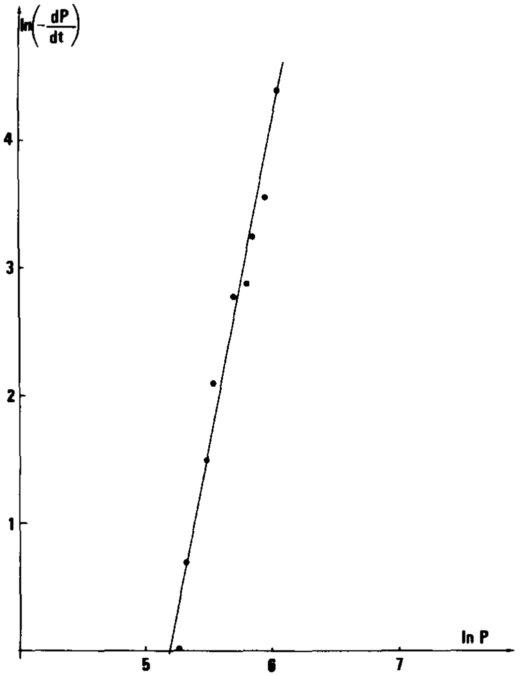

Fig. 4. Carbamate formation at 307 K ($P^0 = 540$ torr, stoichiometric mixture). Graph of $\ln(-dP/dt)$ vs. $\ln P$.

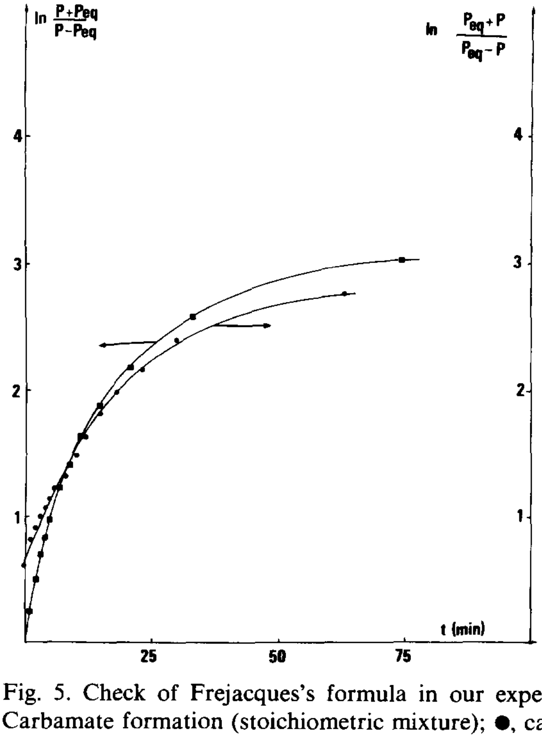

Fig. 5. Check of Frejacques's formula in our experiments ($T = 307$ K, $P^0 = 540$ torr). ■, Carbamate formation (stoichiometric mixture); ●, carbamate decomposition.

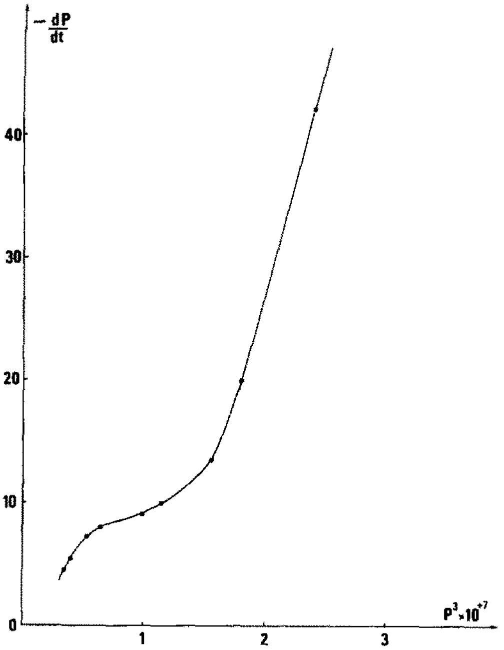

Fig. 6. Representation of our results (carbamate formation at $T = 300$ K, stoichiometric mixture, $P^0 = 350$ torr) according to the kinetic expression of Laurent and Kikindai [9].

KINETICS

Initial kinetic parameters for carbamate formation

As stated above the study of reaction kinetics in the initial conditions offers the means of getting rid of the possible influence of the products. We therefore began by investigating the initial formation of carbamate. The initial partial reaction orders have been determined, in a classical way [10]: the partial order α with respect to A is obtained by running the reaction with an excess of B. The curve P_A vs. t is linearized by plotting $\ln(-\mathrm{d}P_A/\mathrm{d}t)$ vs. P_A, so that $(\mathrm{d}P_A^0/\mathrm{d}t)$ can be determined safely by extrapolating this straight line. Finally $\ln(-\mathrm{d}P_A^0/\mathrm{d}t)$ is plotted as a function of $\ln P_A^0$. As can be seen from Fig. 7, the points fit fairly well on a straight line, the slope of which is close to unity. The same procedure repeated with an excess of A gives the initial partial order β with respect to B, which again is close to unity (Fig. 8). This was checked by using a stoichiometric mixture, which allows the initial overall order to be determined, with a result close to two.

It is then possible to obtain the rate constant k from relation (4), rewritten here

$$\left(\frac{1}{\nu_i}\right)\left(\frac{\mathrm{d}P_i}{\mathrm{d}t}\right) = k\prod_i P_i^{\epsilon_i} \tag{7}$$

Fig. 7. Determination of initial partial order α with respect to CO_2 for carbamate formation.

i.e., given the values found for the initial partial orders

$$\left(\frac{1}{\nu_i}\right)\left(\frac{dP_i^0}{dt}\right) = k^0 P_A^0 P_B^0 \tag{8}$$

We can apply this relationship to the three cases above

$$-\frac{dP_A^0}{dt} = k^0 P_A^0 P_B^0$$

$$-\frac{1}{2}\frac{dP_B^0}{dt} = k^0 P_A^0 P_B^0$$

$$-\frac{dP^0}{dt} = \tfrac{2}{3}k^0 (P^0)^2$$

and we should find the same value of k^0 at a given temperature. For instance at 296 K, the experimental findings are respectively 7.3($\pm$0.2), 7.2($\pm$0.3), 7.0($\pm$0.1) $\times 10^{-4}$ torr^{-1} min^{-1} which is adequate agreement.

Changing the temperature allows the initial activation energy to be determined (Fig. 9), i.e. $E^0 \sim 18$ kcal mol^{-1}.

Kinetic parameters during the course of reaction

For the sake of simplicity, we shall distinguish between "formation" and "decomposition" of ammonium carbamate, according to the initial condi-

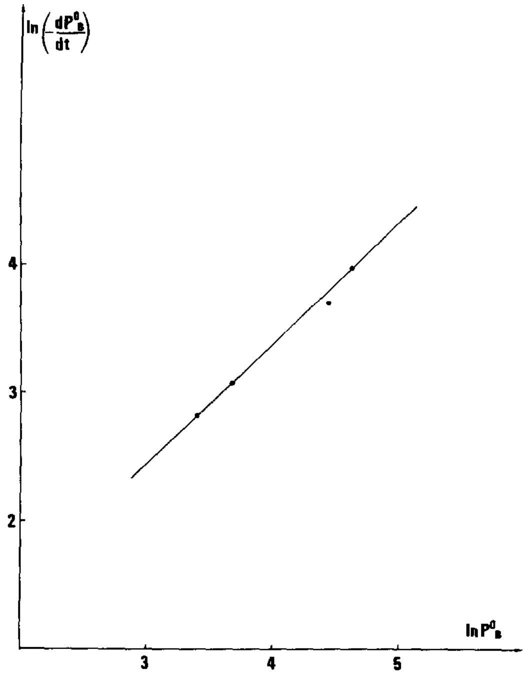

Fig. 8. Determination of initial partial order β with respect to NH_3 for carbamate formation.

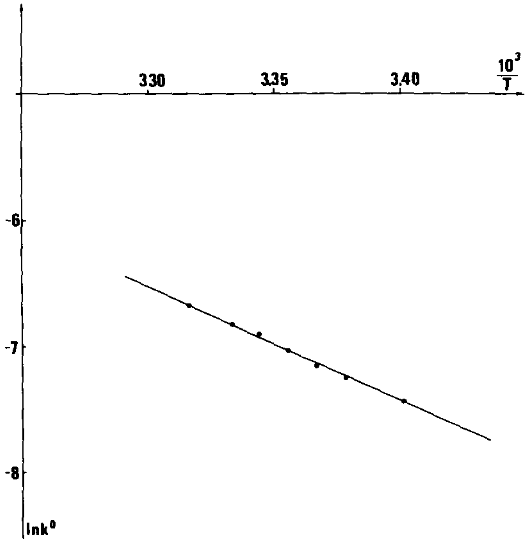

Fig. 9. Arrhenius plot for the determination of initial activation energy for carbamate formation.

TABLE 1

Exploitation of kinetic results during the course of carbamate formation ($T = 302$ K)

t (min)	P (torr)	$P - P_{eq}$ (torr)	$\ln(P - P_{eq})$	$(P - P_{eq})^{-1}$ $\times 10^2$	$(P - P_{eq})^2$ $\times 10^{-4}$	$\lvert dP/dt \rvert$ (torr min^{-1})	$\ln \lvert dP/dt \rvert$
0	480	365	5.90	0.27	–	–	–
1	360	245	5.50	0.41	6.00	80	4.38
2	320	205	5.32	0.49	4.20	35	3.56
3	290	175	5.16	0.57	3.06	25	3.22
4	270	155	5.04	0.65	2.40	17.5	2.86
5	255	140	4.94	0.71	1.96	12.5	2.53
6	245	130	4.87	0.77	1.69	12.5	2.53
7	230	115	4.74	0.87	1.32	8	2.08
11	210	95	4.55	1.05	0.90	5	1.61
15	190	75	4.32	1.33	0.56	4	1.39
27	160	45	3.81	2.22	0.20	1.8	0.59
34	150	35	3.56	2.86	0.12	0.7	−0.36
45	140	25	3.22	4.00	0.06	0.4	−0.92
84	130	15	2.71	6.67	–	–	–
102	125	10	2.30	10.00	–	–	–

tions, although, as we have seen, both opposite reactions occur simultaneously, so that the rate measured by $|dP/dt|$ will be a net rate (all the gaseous mixtures in the experiments below will be stoichiometric).

Formation reaction

Let us take as an example the reaction corresponding to conditions $T = 302$ K, ($P_{eq} = 115$ torr), $P^0 = 480$ torr. Table 1 gives the values of the total pressure P as a function of time t. As we need an algebraic representation of the net rate, we need to look for an expression which has a root for $P = P_{eq}$. The simplest way of finding such an expression is to draw $\ln |dP/dt|$ vs. $\ln(P - P_{eq})$. If a straight line of slope m is found, it will mean that the net rate can be expressed by

$$|dP/dt| = k(P - P_{eq})^m \qquad (9)$$

Such a graph is shown by Fig. 10, from which the value $m = 2$ can be derived. A more accurate check is provided by the representation of $|dP/dt|$ as a function of $(P - P_{eq})^2$: a straight line passing through the origin must be obtained, and is shown by Fig. 11. The slope of this straight line gives $k = 7 \times 10^{-4}$ (± 0.9) torr^{-1} min^{-1}. Another check is made by integrating relation (9), which gives

$$\left(\frac{1}{P - P_{eq}}\right) - \left(\frac{1}{P_0 - P_{eq}}\right) = kt$$

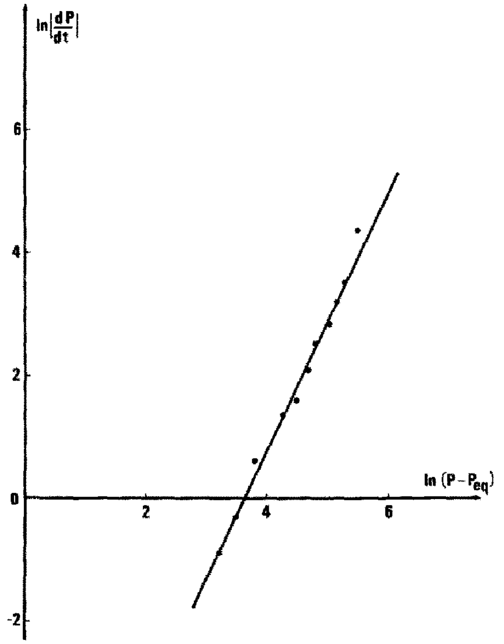

Fig. 10. Determination of the "order" with respect to $P - P_{eq}$ for carbamate formation at 302 K.

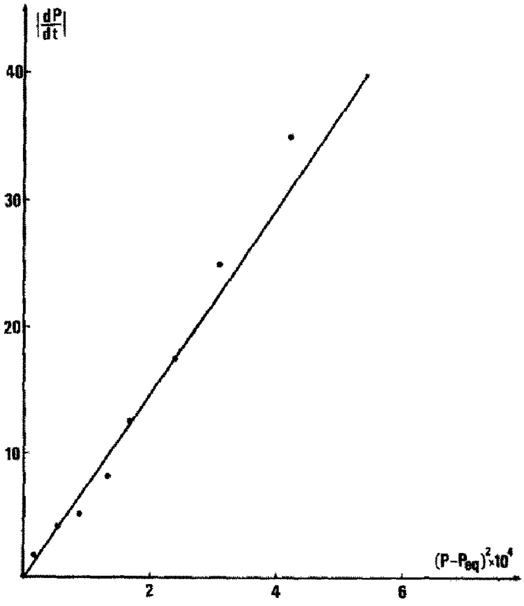

Fig. 11. Carbamate formation: check of $|dP/dt|$ vs. $(P - P_{eq})^2$ ($T = 302$ K).

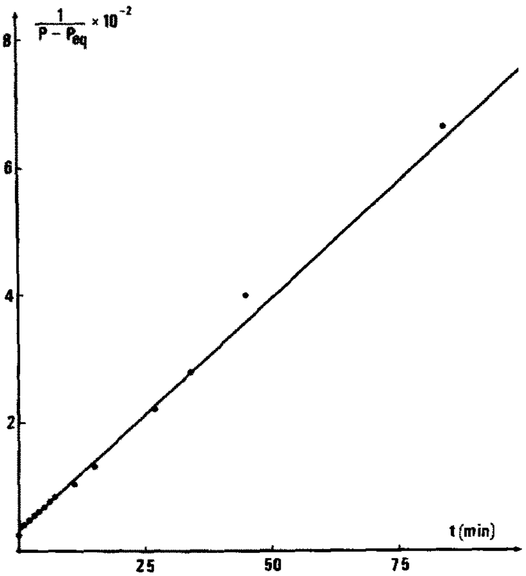

Fig. 12. Carbamate formation: check of $(1/P - P_{eq})$ vs. t $(T = 302$ K).

and, therefore in drawing $1/(P - P_{eq})$ as a function of t: again, a straight line is obtained (Fig. 12), from which a compatible value of k is derived ($k = 7.4 \times 10^{-4}$ (± 0.2) torr^{-1} min^{-1}). This exploitation of our experimental results at different temperatures and initial pressures confirms the value $m = 2$ of the "order" with respect to $P - P_{eq}$ and yields for k the values shown in Tables 2 and 3.

In classical kinetics, the "constant" k would be a function of temperature, and it would be expected to obey the Arrhenius law. However, if, in our case, we evaluate the correlation coefficient between $1/T$ and ln k, we find 0.32 with the "differential" method, and not more than 0.63 with the

TABLE 2

Evaluation of k in formation by the "differential method"

T (K)	$10^3/T$	$k \times 10^{-4}$ (torr^{-1} min^{-1})	ln k	$\Delta k/k = \Delta$ ln k
287	3.484	6.13	−7.39	0.12
290	3.448	8.37	−7.07	0.10
294	3.401	3.75	−7.89	0.17
295	3.389	5.38	−7.53	0.11
296	3.378	4.43	−7.72	0.17
300	3.333	5.02	−7.59	0.14
302	3.311	7.00	−7.26	0.09
305	3.278	10.19	−6.89	0.12
307	3.257	8.80	−7.03	0.17

TABLE 3

Evaluation of k in formation by the "integral method"

T (K)	$10^3/T$	$k \times 10^{-4}$ (torr^{-1} min^{-1})	ln k	$\Delta k/k = \Delta \ln k$
287	3.484	5.75	−7.46	0.15
290	3.448	8.55	−7.06	0.13
294	3.401	3.34	−8.00	0.14
295	3.389	4.78	−7.87	0.09
296	3.378	4.73	−7.65	0.16
300	3.333	4.23	−7.77	0.16
302	3.311	7.40	−7.21	0.02
305	3.278	10.19	−6.89	0.13
307	3.257	8.50	−7.07	0.08

"integral" method. This means that k is not primarily a function of temperature.

Decomposition reaction

As we deal with net rates, that of decomposition should be analogous to that of formation, i.e.

$$\frac{dP}{dt} = k'(P_{eq} - P)^2$$

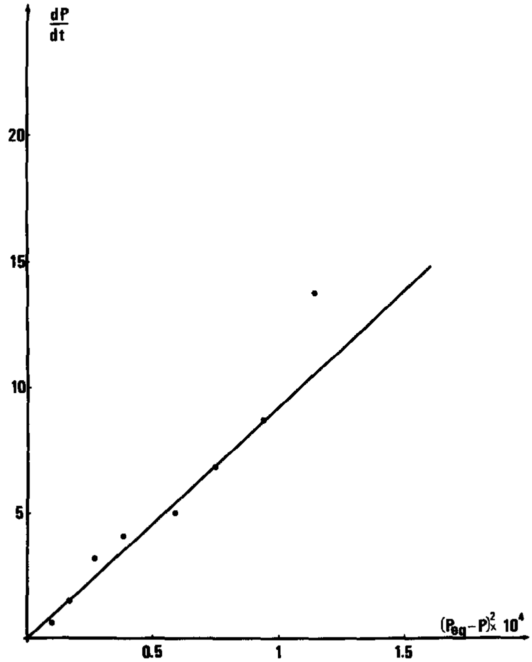

Fig. 13. Carbamate decomposition: check of (dP/dt) vs. $(P_{eq} - P)^2$ ($T = 304$ K).

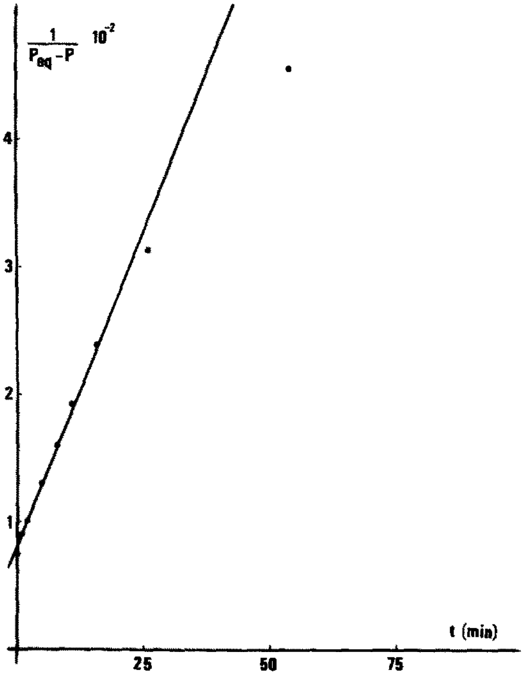

Fig. 14. Carbamate decomposition: check of $(1/P_{\mathrm{eq}} - P)$ vs. t ($T = 304$ K).

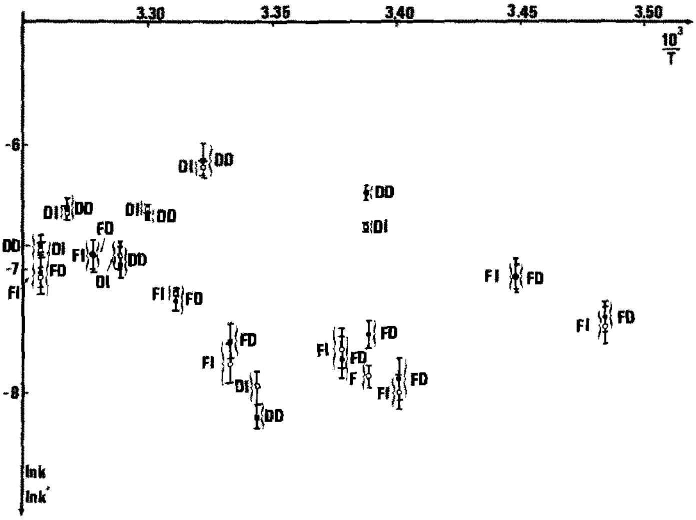

Fig. 15. Representation of ln k vs. $1/T$: ●, formation, "differential" method (FD); ○, formation, "integral" method (FI); ■, decomposition, "differential" method (DD); □, decomposition, "integral" method (DI).

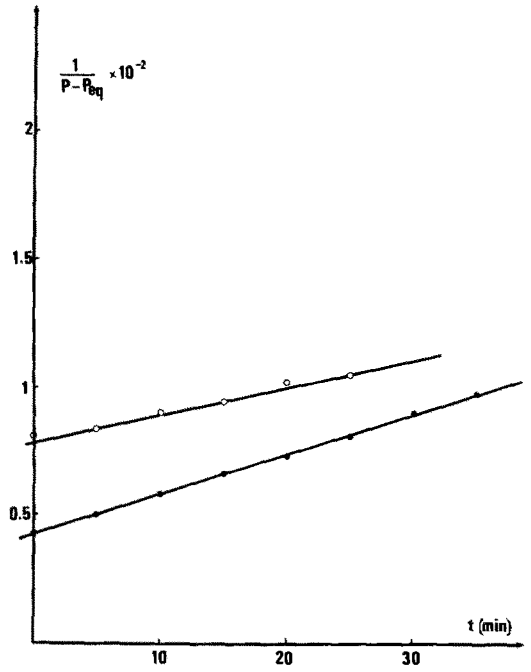

Fig. 16. Application of the kinetic expression $1/(P-P_{eq}) = kt$ + constant to Naumann's results (carbamate formation at 309 K): series VIII [1], series IX [1].

This expression is effectively checked, as shown by Figs. 13 and 14 drawn from an experiment at 304 K ($P_{eq} = 132$ torr). The values of k' which can be derived are similar (10 ± 1.3 torr^{-1} min^{-1}). Again, the correlation coefficient between $1/T$ and ln k' is quite low: 0.10 for the "differential"

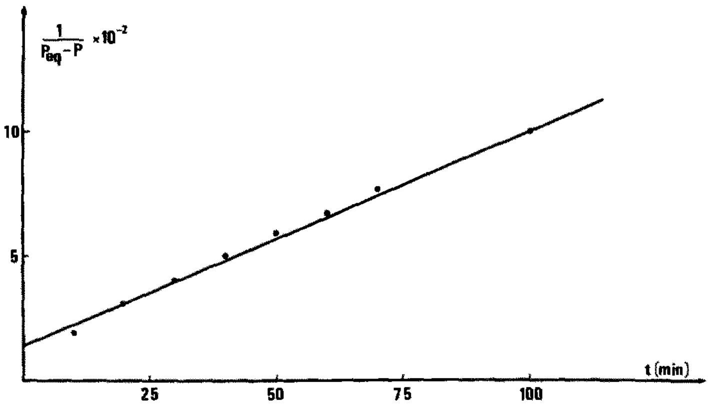

Fig. 17. Application of the kinetic expression $(1/(P_{eq}-P) = kt$ + constant to Naumann's results (carbamate decomposition at 315 K) [1].

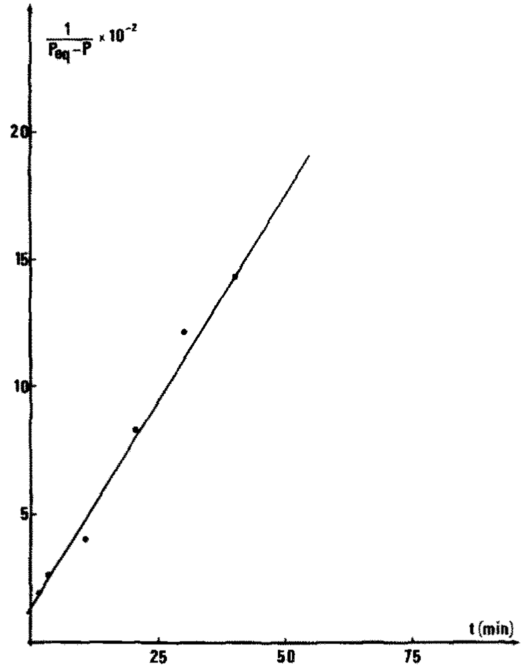

Fig. 18. Application of the kinetic expression $1/(P_{eq} - P) = kt +$constant to Janjic's results (carbamate decomposition at 295.3 K) [6].

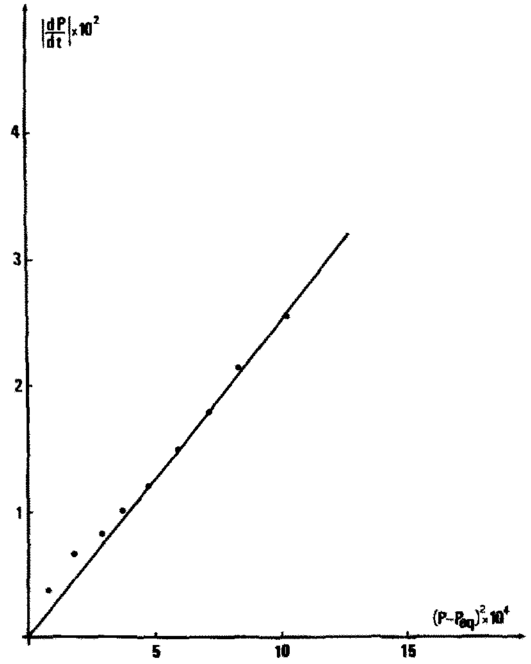

Fig. 19. Application of the kinetic expression $dP/dt = k(P - P_{eq})^2$ to the results of Laurent and Kikindai [9] ($T = 309$ K).

method, and 0.19 for the "integral" method, so that k' does not appear as primarily dependent on temperature. Moreover, the significance of a net rate is that k' should be equal to k. Figure 15 allows comparison of both sets of values, their logarithms, with their uncertainty segment, being plotted vs. $10^3/T$. It confirms the absence of correlation between these variables, and the comparable order of magnitude of k and k' (with perhaps a slight systematic predominance of k').

It is interesting to check whether the results of the older kinetic studies conform to the kinetic expression that we propose. Figures 16 and 17 correspond to three series of data from Naumann [1], Fig. 18 to a series of data from Janjic [6], and Fig. 19 to a series of data from Laurent and Kikindai [9]. It can be seen that they are all in good agreement with the proposed kinetics. Interestingly, the straight lines of Fig. 16 are not parallel, although they have been obtained at the same temperature. This confirms that k is not a function of temperature alone.

PROPOSED MECHANISMS OF AMMONIUM CARBAMATE FORMATION AND DECOMPOSITION

Initial kinetics

The partial orders equal to unity with respect to each reactant can be accounted for by the scheme already given

$$A + B \rightarrow D \tag{1a}$$

$$D + B \rightarrow C \tag{1b}$$

assuming now that reaction (1a) is rate determining. The intermediate compound D which is carbamic acid NH_2–COOH has never been isolated or even characterized, so that it is a priori difficult to prove its transitory existence. The activation energy that we found for reaction (1a) 18 kcal mol^{-1} depends on the operating conditions. As previously noted, water will accelerate this reaction [13], whereas "alcohol vapours" [11] exert an inhibiting influence.

Kinetics during the course of reaction

It is shown by our experimental study that the net rate cannot be in the form [4] common in classical kinetics, but is proportional to ΔP^2, ΔP being the "driving force" in Fig. 1. This feature evokes the kinetics of a phase change, such as crystallization and dissolution. This idea, relatively new in gas–solid reactions, has already been put forward, but without quantitative substantiation in the case of ammonium chloride formation from gaseous HCl and NH_3 [14] and even of ammonium carbamate [11]. A net rate proportional to $\Delta c^2(\Delta c = c - c_{eq})$ is common in crystallization from solution [15,16], e.g. crystallization of potassium sulfate [17–20], of hydrargillite [21], and of calcium carbonate [22,23].

This second "order" law is usually interpreted by crystal growth kinetics [24], and more precisely, of a spiral step centred at a screw dislocation [23]. We therefore propose to apply this model to ammonium carbamate crystallization from the seeds formed by the initial steps (1a) and (1b). The "constant" k of expression (9), which we know does not depend primarily on temperature should be examined closer. Indeed, it is usual in studies on crystallization to write it in the form: $k = k''S$, where S is the crystal area. This area does not appreciably vary in the course of an experiment, but changes from one experiment to another (which is confirmed visually, since the region where the crystals form is not always the same). In this respect, it is logical to assume that S is larger (at least at the beginning) during decomposition than during formation, which explains the localization of points on Fig. 15. Moreover the area extension is probably not the only factor which has to be taken into account: the physical state of the surface itself (e.g. the existence of defects, dislocations, etc.) is likely to be important, so that k'' itself is a function of parameters difficult to rationalize a priori. Micrographs of the surface could give a qualitative confirmation of their intervention.

In conclusion, the kinetics of ammonium carbamate formation and decomposition have been studied manometrically. During the course of the reaction the two opposite reactions which occur simultaneously lead to a net rate proportional to the square of $P - P_{eq}$ (P, total pressure of the stoichiometric mixture of gases). This could be interpreted by a mechanism where the crystal growth (and decrease) is rate determining.

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