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# The Effect of Pressure on the Rate of the Acid-catalyzed Hydration of Propylene

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In order to confirm whether a water molecule (or molecules) is held in a protonated activated complex by electrostatic interaction or by a partial valence bond, the pressure dependency of the activation volume, $\Delta V^{\ast}$, for the hydration of propylene was measured at 180°C. The pressure effect on the rate of the hydration of propylene was studied in such dilute sulfuric acid solutions of a 0.0000108 mole fraction (0.00060N under S.T.P.) that the dielectric constant, $D$, and the density of pure water could be replaced for those of the reacting solution. The absolute value of the $\Delta V^{\ast}$ decreases steeply from 19 m$l$/mol at 300 kg/cm$^2$ to 4 m$l$/mol at 5000 kg/cm$^2$. The activation energies and entropies, obtained from the temperature dependency of the reaction rate, are 22.7 kcal/mol and $-16.6$ e.u./mol respectively at 1000 kg/cm$^2$ and 21.9 kcal/mol and $-17.0$ e.u./mol respectively at 3000 kg/cm$^2$. The $\Delta V^{\ast}$ is approximately proportional to the $-\partial D/D^2\partial p$ value, ($D$: dielectric constant of medium; $p$: pressure), which follows from the Krichevski equation; hence, it was concluded that the contraction of water around an activated complex by electrostatic interaction contributes to the $\Delta V^{\ast}$ and that a water molecule (or molecules) is held in the activated complex by electrostatic interaction. The case of a water molecule being held by a partial valence bond was discussed in terms of the molar volumes of the reactants.

Investigations of the transition state of the acid-catalyzed hydration of olefins have been made by several workers.[1-3] It has been reported that the rate-determining step, for simple olefins, is either the formation of a carbonium ion, which is rapidly captured by water,[1] or a proton transfer from a hydrated proton to an olefin.[4] In any case, the transition state contains perhaps one or more molecules of water. In order to determine the rate-determining step, it is valuable to investigate the behavior of water molecules in the transition state.

Baliga and Whalley[5] studied the pressure effects on the rates of the hydration of ethylene, propylene, and isobutene; they obtained activation volumes of $-15.5$ m$l$/mol at 180°C, $-9.6$ m$l$/mol at 100°C, and $-11.5$ m$l$/mol at 35°C. They concluded that, at the transition states for these reactions, the partial covalent bond is formed between a protonated olefin and a water molecule. The proposed state, however, is based on the assumption that there is only a small difference between the contraction of water around an activated complex and the electrostriction of the proton in the formation of the transition state.

On the other hand, Taft[1] found that the logarithm of the rate of the hydration of isobutene is proportional to the acidity function, $-H_0$, and concluded that the transition state is a "free" carbonium ion. By "free" carbonium ion he meant an ion hydrated only by ion-dipole interaction, without any strong covalent interactions between the ion and a water molecule. This mechanism was, however, proposed on the basis of the Zucker-Hammett hypothesis, and this hypothesis has been shown not always to be applicable to the reactions thus far examined.[6-9] Moreover, this mechanism presents another contradiction: the ratio of the rate constant in $D_2O$ to that in $H_2O$ was actually close to unity, although the values of the ratio for most A-1 reactions are between two and three.

In order to confirm whether a water molecule (or water molecules) is held in the protonated activated complex by electrostatic interaction or by a partial valence bond, the present investigation into the pressure dependency of the activation volume, $\Delta V^{\ast}$, for the hydration of propylene was undertaken at 180°C. At 180°C the dielectric constant of water, which affects the electrostatic interaction, increases considerably with the pressure, but the decrease in the molar volume of water is small,—*i.e.*, the decrease in the radius of a water molecule is small. If the electrostatic bonds between the protonated activated complex and water result in a larger contraction of water around an activated complex than that around the hydrated proton,—if, *i.e.*, the principal term contributing to $\Delta V^{\ast}$ is a change in the contraction of water between an activated complex and a hydrated proton, —the absolute value of $\Delta V^{\ast}$ will decrease considerable with the pressure as a result of the increase in the dielectric constant with the pressure. On the other hand, if the formation of a partial valence bond between a protonated propylene and a water molecule contributes to the activation volume, $\Delta V^{\ast}$, the decrease in the absolute value of $\Delta V^{\ast}$ with the pressure will be small since the decrease in the molar volume of water with pressure is small.

## Experimental

*Materials.* The water used in this experiment was purified by passing it through two kinds of ion exchange-resin; it was subsequently distilled twice to remove fine particles of the exchange-resins, which have a superior catalytic activity

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1) R. W. Taft, Jr., *J. Amer. Chem. Soc.*, **74**, 5372 (1952).

2) C. A. Bunton and V. J. Shiner, Jr., *ibid.*, **83**, 42 (1961). *ibid.*, **83**, 3215 (1961).

3) E. L. Puelee and R. W. Taft, Jr., *ibid.*, **78**, 5807 (1956).

4) F. A. Long and M. A. Paul, *Chem. Revs.*, **57**, 935 (1957).

5) B. T. Baliga and E. Whalley, *Can. J. Chem.*, **42**, 1019 (1964); *ibid.*, **43**, 2453 (1965).

6) J. F. Bunnett, *J. Amer. Chem. Soc.*, **83**, 4956 (1961).

7) R. W. Taft, Jr., N. C. Deno, and P. S. Skell, *Ann. Rev. Phys. Chem.*, **9**, 306 (1958).

8) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, New York (1959).

9) H. Takaya, N. Todo, and T. Hosoya, This Bulletin, **42**, 2748 (1969).

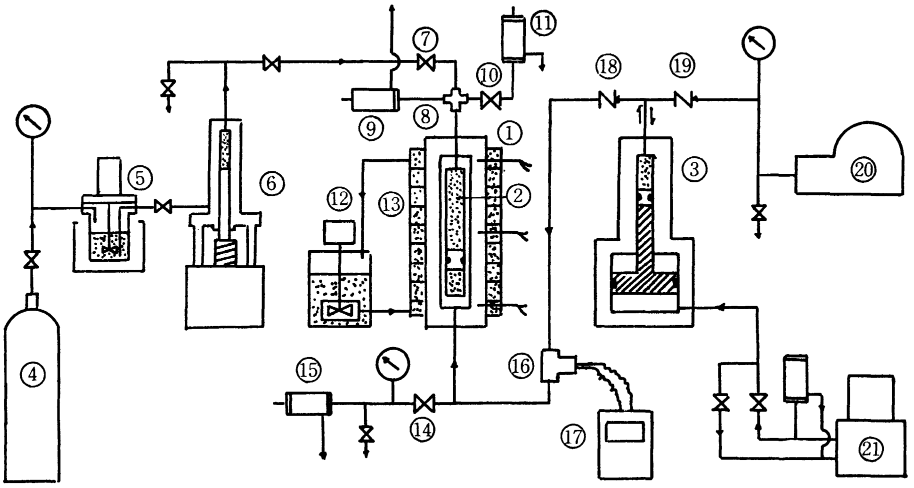

Fig. 1. Equipment used under pressure.

1: Reaction vessel 2: Reactor 3: Pressure intensifier
4: Cylinder of propylene 5: Propylene absorber 6: Injector of reacting solutions
7: Valve 8: Cross fitting 9: Safety valve
10: Valve 11: Relief valve 12: Circulater of heated oil
13: Jacket of reactor for heating 14: Valve 15: Relief valve
16: Manganin pressure cell 17: Pressure recorder 18, 19: Check valve
20: Pump for charging silicone oile 21: Pump for driving intensifier

for the hydration of olefin. The propylene (extra-pure grade), obtained commercially, and the sulfuric acid (guaranteed reagent) were used without further purification.

*Apparatus and Procedure.* The equipment used is shown in Fig. 1, while the details of the pressure technique were described in an earlier paper.[10] The reacting solution in the reactor (2), which is contained in a high-pressure vessel (1), can be repeatedly replaced at chosen reaction temperatures under a pressure of 300 kg/cm². The reacting solutions were prepared by dissolving propylene into aqueous acid in a pressure vessel (5) at 0°C under high pressures (up to 8 atm); they were then injected into the reactor (2), kept at chosen reaction temperatures under the pressure of 300 kg/cm² by using a high-pressure injector (6). The reactor (2) was constructed so as to keep the solution in contact only with Teflon. The mole fraction of the propylene dissolved as the reactant was varied from 0.006 to 0.0010

*Analysis.* The progress of the hydration of propylene was followed by analyzing the product extracted at fixed intervals. The gaseous propylene in the products was measured by a gas burette, while the amount of propylene dissolved in the products was determined by gas chromatography. The column used for this measurement was 2 m in length, and 4 mm in dia., and it was packed with 25% P.E.G. 1500 on celite 545 (60-80 mesh).

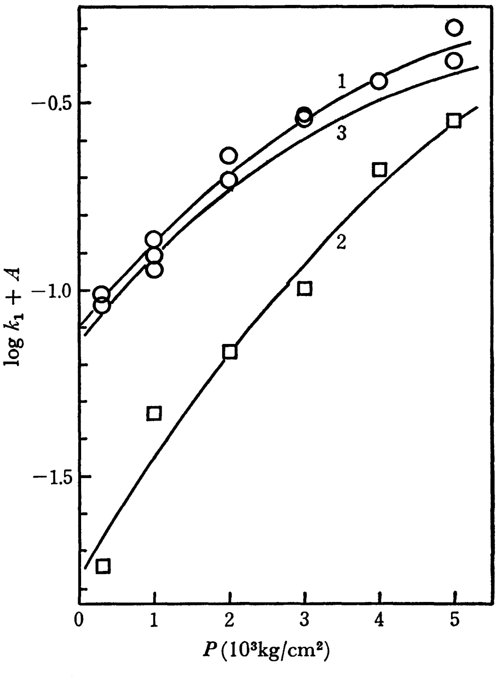

Fig. 2. Effect of pressure on the rate of hydration of propylene at 180°C. The curves 1, 2, and 3 correspond to Eqs. (2), (3), and (4) resperctively.
Curve 1: in aqueous sulfuric acid, $A=0$.
Curve 2: in aqueous solution without acid catalysis, $A=0.6$.
Curve 3: $\log K_{1C}$, A=0.

## Results

The reaction was the first order in propylene,[5] and the rate constant, $k_1$, was calculated by the usual equation (1):

$$\ln x = -k_1 t + \text{constant} \tag{1}$$

where $x$ is the ratio of the mole fraction of the unreacted propylene at the reaction time, $t$, to the initial mole fraction. For the reactions in the dilute sulfuric acid solution of a mole fraction 0.0000108 (0.00060N under S.T.P.) at 180°C, the correlation of $\log k_1$ with the pressure, $p$, was as is shown in Fig. 2, where the $\log k_1$ increases from $-1.0$ at 300 kg/cm² to $-0.3$ at 5000 kg/cm² and is represented by Eq. (2):

$$\log k_1 = -1.109 + 0.245 \times 10^{-3}p - 0.0182 \times 10^{-6}p^2 \tag{2}$$

In the present work, considerably diluted acid was used as the catalyst since the dielectric constant and the density of a diluted acid solution could be replaced with

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[10] T. Hosoya, T. Minegishi, H. Takaya, N. Todo, and M. Yoneoka, *Tokyo Kogyo Shikensho Hokoku*, **64**, 499 (1969).

those of pure water. Therefore, it was necessary to measure the rate for the solution consisting of pure water and propylene. As is shown in Fig 2, it was observed that the reaction without any acid catalysts proceeds, though the rate, $k_{1w}$, was much lower than that for the solution with an acid catalyst. The $\log k_{1w}$ was represented by Eq. (3):

$$\log k_{1w} = -2.371 + 0.347 \times 10^{-3}p - 0.0203 \times 10^{-6}p^2 \quad (3)$$

Accordingly, the correct rate constant, $k_{1c}$, with an acid catalyst was calculated by subtracting those of $k_{1w}$ from $k_1$. In Fig. 2 the $\log k_{1c}$ is also plotted against $p$, its dependence on $p$ can be represented by Eq. (4):

$$\log k_{1c} = -1.144 + 0.247 \times 10^{-3}p - 0.0203 \times 10^{-6}p^2 \quad (4)$$

In Fig. 3 the relation between the activation volume, $\Delta V^{\ne}$, as defined by Eq. (5), and the reacting pressure is shown.

$$\Delta V^{\ne} = -2.303RT\frac{\partial \log k_1}{\partial p} \quad (5)$$

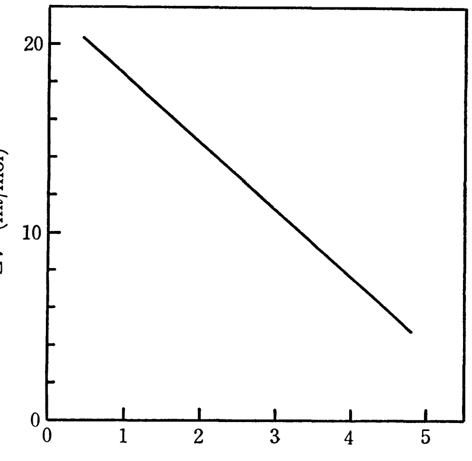

Fig. 3. Effect of pressure on volume of activation for the acid-catalyzed hydration of propylene in water at 180°C.
$-\Delta V^{\ne}=21.9-3.6\times10^{-3}p$ (m$l$/mol)

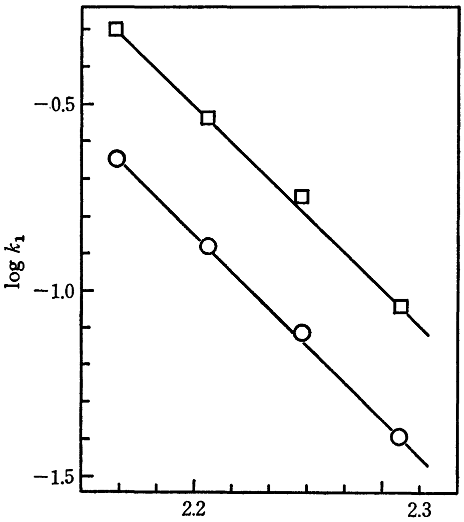

Fig. 4. Effect of temperature on the rate of the acid-catalyzed hydration of propylene. ○: at 1000 kg/cm². □: at 3000 kg/cm².

This figure indicates that the absolute values of the activation volume, the pressure dependency of which is represented by Eq. (6), decrease steeply with the pressure as the same manner as in the case of the hydration of ethylene observed by Baliga at 180°C.[5)] However, the absolute value obtained at 180°C under 300 kg/cm², 19 m$l$/mol, is twice as large as the value, 9.6 m$l$/mol, obtained by Baliga[5)] for propylene at 100°C under about 1 kg/cm².

$$-\Delta V^{\ne} = 21.9 - 3.6\times10^{-3}p \ (\mathrm{m}l/\mathrm{mol}) \quad (6)$$

The temperature dependency of the reaction is shown by Arrhenius plots in Fig. 4. The activation energies and entropies are 22.7 kcal/mol and −16.6 e.u./mol respectively at 1000 kg/cm² and are 21.9 kcal/mol and −17.0 e.u./mol respectively at 3000 kg/cm², where the entropies are calculated in the same manner as in Baliga's report.[5)]

## Discussion

As was shown in the preceding paper[9)] the mechanism of the acid-catalyzed hydration of propylene can be represented by Eq. (7) and Eq. (8):

$$C_3H_6 + H^+\cdot h_2H_2O + (h_1-h_2)H_2O \overset{K_1}{\rightleftarrows} [C_3H_6\cdot H^+\cdot h_1H_2O]^{\ne} \quad (7)$$

$$[C_3H_6\cdot H^+\cdot h_1H_2O]^{\ne} \longrightarrow C_3H_7OH + H^+\cdot h_2H_2O + (h_1-h_2-1)H_2O \quad (8)$$

where $h_1$ and $h_2$ are the hydration numbers of the activated complex and the proton respectively; the hydration number of propylene has been considered to be zero. The activation volume for the reaction represented by Eq. (7) can be defined by Eq. (9)[11)]:

$$\Delta V^{\ne} = \bar{V}_{\mathrm{act.}} - \bar{V}_{\mathrm{prop.}} - \bar{V}_{\mathrm{h.p.}} - (h_1-h_2)\bar{V}_w \quad (9)$$

$$= \Delta V_{\mathrm{act.}} - \Delta V_{\mathrm{H^+}} \quad (10)$$

where $\bar{V}_{\mathrm{act}}$, $\bar{V}_{\mathrm{prop.}}$, $\bar{V}_{\mathrm{h.p.}}$, and $\bar{V}_w$ are the partial molar volumes of the activated complex, propylene, the hydrated proton, and water respectively, and where $\Delta V_{\mathrm{act.}}$ and $\Delta V_{\mathrm{H^+}}$ are defined by Eq. (11) and Eq. (12) respectively:

$$\Delta V_{\mathrm{act.}} = \bar{V}_{\mathrm{act.}} - \bar{V}_{\mathrm{prop.}} - h_1\bar{V}_w \quad (11)$$

$$\Delta V_{\mathrm{H^+}} = \bar{V}_{\mathrm{h.p.}} - h_2\bar{V}_w \quad (12)$$

Here, the volume change, $\Delta V_{\mathrm{H^+}}$, is the electrostriction of the proton. In connection with $\Delta V_{\mathrm{act.}}$, it is convenient to split it into two terms: $\Delta_1 V_{\mathrm{act.}}$, which is the change in the volume of the reacting molecules when they form the transition state, and $\Delta_2 V_{\mathrm{act.}}$, which is the accompanying change in the volume of the surrounding liquid water, arising principally from the change in the contraction of water around an ion by means of electrostatic interaction. Equation (10) can, then, be rewritten as Eq. (13):

$$\Delta V^{\ne} = \Delta_1 V_{\mathrm{act.}} + \Delta_2 V_{\mathrm{act.}} - \Delta V_{\mathrm{H^+}} \quad (13)$$

According to Baliga and Whalley, the principal term contributing to the $\Delta V^{\ne}$ is $\Delta_1 V_{\mathrm{act.}}$, and the contribution

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11) S. D. Hamann, "High Pressure Physics and Chemistry," Vol. 2, ed. by R. S. Bradley, Academic Press, London and New York (1963), p. 165.

of the $(\Delta_2 V_{\text{act.}} - \Delta V_{\text{H}^+})$ term to the $\Delta V^{\ast}$ may be very small. Their consideration, however, is based on the assumption that the size of the activated complex is larger than that of $H_3O^+$, though it is known that the formula of the hydrated proton is not $H_3O^+$, but $H^+ \cdot h_2 H_2O$, where $h_2$ is, *e.g.*, about 4 at 25°C. It seems, therefore, more likely that the size of the ionic activated complex is smaller than that of the hydrated proton. It is probable, then, that $\Delta_2 V_{\text{act.}}$ is smaller than $\Delta V_{\text{H}^+}$ and that $\Delta_1 V_{\text{act.}}$ is negligibly small; the principal term contributing to the $\Delta V^{\ast}$ is $(\Delta_2 V_{\text{act.}} - \Delta V_{\text{H}^+})$.

Let us now discuss which of the two cases is related to the observed large decrease in the absolute value of the activation volume with the pressure: the case 1, where the term contributing to $\Delta V^{\ast}$ is $(\Delta_2 V_{\text{act.}} - \Delta V_{\text{H}^+})$; and the case 2, where the term contributing to $\Delta V^{\ast}$ is $\Delta_1 V_{\text{act.}}$

Case 1. In order to discuss the contraction of water around an ion, the method of the calculation of the contraction must first be considered. The contraction is expressed by Krichevski equation, which follows from Born's model:

$$\Delta V_{\text{el.}} = -\frac{z^2 e^2 \partial D}{2rD^2 \partial p} \qquad (14)^{11)}$$

where $\Delta V_{\text{el.}}$ denotes the contraction of a medium of the dielectric constant, $D$, around a sphere of the radius, $r$, carrying a charge of $ze$, e being the electronic charge, and $z$, an intergal number, and where $p$ is the pressure. Hamann[11)] derived the equation of the contraction by considering the pressure dependency of $r$. In order to calculate the correct value of the contraction, the arrangements of the water molecules at the nearest neighbor of an ion must be taken into account.[12)] The arrangement effect is especially important in the case of a small ion.[12)] However, there have been reported none of the experimental data necessary to evaluate the arrangements of the water molecules and the pressure dependency of $r$ at high temperatures and pressures. Therefore, in this paper it is assumed, neglecting these effects, that $\Delta V_{\text{el.}}$ is proportional to the $-\partial D/D^2 \partial p$ value. This assumption is partly supported by the fact that the radius of a protonated activated complex is large and by the following facts. The variation of the radius of *n*-heptane, even at 300°C, is only about 10 per cent with the increase in pressure from 1000 kg/cm² to 5000 kg/cm², since their molar volumes under pressures of 1000 kg/cm² and 5000 kg/cm² are 164 m*l* and 129 m*l* respectively.[13)] Those molar volumes are not greatly different from that under S.T.P. (145 m*l*). Therefore, it may be deduced that the variation in the radius of propylene is also small, since the molar volume of propylene, 79 m*l*, at 180°C under a pressure of 1000 kg/cm² is not greatly different from that in the liquid state, 60 m*l*.

If the principal terms contributing to $\Delta V^{\ast}$ are the $(\Delta_2 V_{\text{act.}} - \Delta V_{\text{H}^+})$ terms, $\Delta V^{\ast}$ should be proportional to the $-\partial D/D^2 \partial p$ value, because $\Delta_2 V_{\text{act.}}$ and $\Delta V_{\text{H}^+}$ are both proportional to the $-\partial D/D^2 \partial p$ value. Figure 5 shows that the observed activation volumes, in which the values observed by Baliga at 100°C have been included, are approximately proportional to the $-\partial D/D^2 \partial p$ value. Here, the values, $-\partial D/D^2 \partial p$, for pure water were calculated by the Quist equation,[14)] and the density of water, which is necessary to evaluate the dielectric constant, was obtained from Sharp's report.[15)] From this figure it may be reasonable to conclude that the main contribution to the $\Delta V^{\ast}$ consists of the $(\Delta_2 V_{\text{act.}} - \Delta V_{\text{H}^+})$ terms; that is, water molecules (or a water molecule) are held in an activated complex by electrostatic interaction.

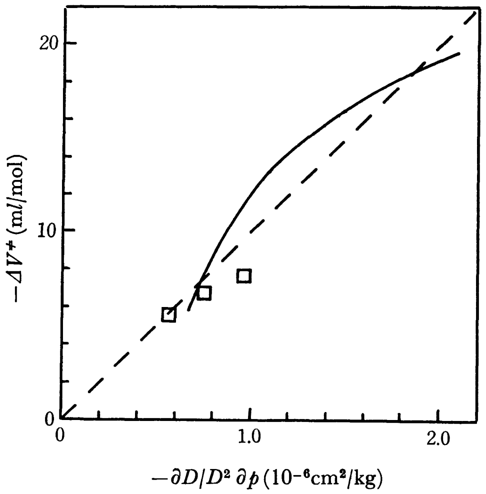

Fig. 5. $-\Delta V^{\ast}$ *versus* $-\partial D/D^2 \partial p$.
—: present results.
☐: Baliga, at 100°C. Ref. 5.

Case 2. By the following procedure it can be shown that the Case 2 is unlikely. If the principal term contributing to $\Delta V^{\ast}$ is $\Delta_1 V_{\text{act.}}$, the observed $\Delta V^{\ast}$ should be caused by contraction, $\delta l$, from the length of a van der Waals bond between a propylene and a water molecule into that of a partial valence bond between a protonated propylene and a water molecule. Therefore, the activation volume, $\Delta V^{\ast}$, can be approximately represented by Eq. (15):

$$\Delta V^{\ast} = -S\delta l \qquad (15)$$

where $S$ is a cross-sectional area for a water molecule. The observed $-\Delta V^{\ast}$ value, 18 m*l*/mol, at a pressure of 1000 kg/cm² is nearly equal to a molar volume of water under the same conditions, 19.1 m*l*/mol.[15)] This means, from Eq. (15), that a water molecule is completely embraced in a protonated propylene upon the formation of the activated complex. From the above conception of the activation process, the $-\Delta V^{\ast}$ value at a pressure of 5000 kg/cm² should be a molar volume of water, 17 m*l*/mol.[15)] However, the observed $-\Delta V^{\ast}$ value at a pressure of 5000 kg/cm² is only 4 m*l*/mol. The large discrepancy shows that the case 2 is unlikely.

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[12)] B. E. Conway, J. E. Desnoyers, and A. C. Smith, *Phil. Trans. Roy. Soc. London*, **256**, 389 (1964).

[13)] A. D. Doolittle, *Chem. Eng. Progr. Symp. Ser.*, **59**, 1 (1963).

[14)] A. S. Quist and W. L. Marshall, *J. Phys. Chem.*, **69**, 3165 (1965).

[15)] W. E. Sharp, *University of California Radiation Laboratory Report* UCRL-7118 (1962).