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The Measurement of Reaction Rates under Pressure by using a Manganin Pressure Gauge

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An apparatus capable of following reaction rates under pressure without sampling has been designed and constructed. The pressure change due to the progress of a reaction in a closed system could be accurately measured to about 0.08 atm by means of a "fixed bridge" combined with a manganin pressure gauge, in which the unbalanced e.m.f. generated at a constant bridge current was potentiometrically determined to 0.1 μV. The rates of the acid-catalyzed inversion of sucrose and the base-catalyzed decomposition of diacetone alcohol, with the expansion in volume and the contraction respectively, were measured in order to verify the applicability of this apparatus. The agreement between the results obtained by this method and those obtained by the analytical method was satisfactory. From these results, it has been confirmed that the method is sufficiently applicable to the measurement of reaction rates under pressure.

The techniques for measuring reaction rates under pressure may be generally classified into two kinds. One is the method usually employed, which requires the sampling of the reaction mixture for analysis with or without the release of pressure, while the other is that which immediately determines the reaction rates without any sampling by following the change in the physical properties of the reaction mixture due to the conversion. The latter method is essentially restricted in the range of its application by the character of the measured reaction, but if a suitable means of following the change is found, then it becomes very useful. A conductance method is typical of this kind of means and has been employed conveniently for the measurement of the rates of several solvolyses under pressure.[1] The technique of following the rate by using a manganin pressure gauge, which is called the piezometric method (or occasionally the dilatometric method), is of the same kind and has recently been used by several workers in studying some liquid-phase reactions.[2–4] Since this method involves measuring the pressure change caused when the reaction takes places in a closed pressure vessel, the desired accuracy should be insured in the measurement of the pressure.

As was pointed out by Withey and Whalley,[3] the pressure change caused by the reaction results in a change in the rate constant, a change dependent on the magnitude of the volume of activation, therefore, the extent of pressure change during the kinetic measurement, which may be allowed for measuring the rate constant with the same accuracy, is entirely limited by the absolute value of this parameter, being small for the reaction with a large value, but large for that with a small one. For instance, in order to obtain the rate constant with an accuracy of 1 per cent for the reaction whose volume of activation is ±5 cm^3/mol, the total pressure change measured must be less than 50 atm; hence, it is desired that the sensitivity of the pressure in the measurement is greater than 0.5 atm.

The "fixed-bridge" method has been employed in the present work because it is most suitable for measuring by means of a manganin gauge coil, the resistance change dependent on such a small pressure change. This method, first employed by Adams *et al.*,[5,6] is essentially based on the measurement of the unbalanced electromotive force (e.m.f.) generated in a Wheatstone bridge with four fixed arms and containing the gauge coil when at a constant bridge current; it is more accurate than directly measuring the resistance change itself. Withey and Whalley[3] also adopted the same method in principle and made an apparatus capable of measuring the pressure change automatically. The measurements of the e.m.f. in this work were carried out with a potentiometer in order to determine exact absolute values comparable

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[1] J. Buchanan and S. D. Hamann, *Trans. Faraday Soc.*, **49**, 1425 (1953); J. B. Hyne, H. S. Golinkin, and W. G. Laidlaw, *J. Amer. Chem. Soc.*, **88**, 2104 (1966); H. S. Golinkin, I. Lee, and J. B. Hyne, *ibid.*, **89**, 1307 (1967); A. B. Lateef and J. B. Hyne, *Can. J. Chem.*, **47**, 1369 (1969); B. T. Baliga and E. Whalley, *J. Phys. Chem.*, **73**, 654 (1969); B. T. Baliga and E. Whalley, *Can. J. Chem.*, **48**, 528 (1970); D. L. Gay and E. Whalley, *ibid.*, **48**, 2021 (1970); M. J. Mackinnon, A. B. Lateef, and J. B. Hyne, *ibid.*, **48**, 2025 (1970).

[2] F. M. Merrett and R. G. W. Norrish, *Proc. Roy. Soc.* (London), **A 206**, 309 (1951); C. Walling and J. Pellon, *J. Amer. Chem. Soc.*, **79**, 4776 (1957); C. Walling and J. Pellon, *ibid.*, **79**, 4782 (1957).

[3] R. J. Withey and E. Whalley, *Trans. Faraday Soc.*, **59**, 895 (1963).

[4] R. J. Withey and E. Whalley, *ibid.*, **59**, 901 (1963).

[5] L. H. Adams, E. D. Williamson, and J. Johnston, *J. Amer. Chem. Soc.*, **41**, 12 (1919).

[6] L. H. Adams, R. W. Goranson, and R. E. Gibson, *Rev. Sci. Instr.*, **8**, 230 (1937).

with those estimated theoretically.

The present paper will describe a technique for following the reaction rate piezometrically and will present some results obtained for the acid- and base-catalyzed reactions under pressure.

Apparatus

A schematic diagram of the high-pressure apparatus used is shown in Fig. 1. It consists principally of four components: a pressure vessel, a manganin pressure gauge, a Bourdon gauge, and a high-pressure hand-operated pump. The pressure vessel, with a capacity of about 180 cm^3, was a cylinder made of SUS-27 stainless steel, 11 cm in diameter and 24 cm in length; it was sealed by means of an O-ring, with a back-up ring made of Teflon. The reaction vessel was a hypodermic syringe with a Teflon plug, with a capacity of about 90 cm^3; it was put in a pressure vessel filled with silicone oil as the pressure-transmitting fluid. The manganin pressure gauge used was that made by the Harwood Engineering Co., Inc.; it consisted of two non-inductively would manganin coils which both had 120±0.1 ohm resistance at atmospheric pressure. The one was a pressure-active coil which had a pressure coefficient of 2.446×10^{-6} atm^{-1}; it was exposed to the pressure system, but was enclosed by a bronze bellows filled with methyl butane in order to isolate it from the pressure fluid. The other, a compensating coil, was located in the cap of the gauge cell. These coils were connected in series to form a Wheatstone bridge with two other precise resistance coils.

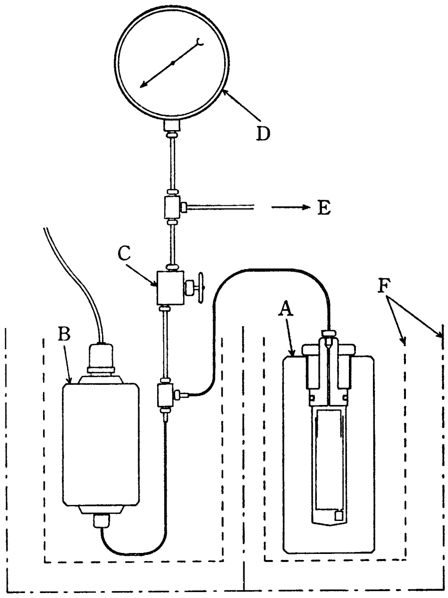

Fig. 1. Schematic diagram of the high pressure apparatus. A: Pressure vessel, B: Manganin pressure gauge, C: Valve, D: Bourdon gauge, E: Pressure pump, F: Thermostat.

The pressure vessel and the manganin gauge were separately immersed in each thermostat, which was doubly thermostatted and was capable of controlling the temperature to 0.001°C; its temperature was measured to 0.001°C by means of a precise Beckmann thermometer. It has been found that the pressure coefficient of the resistance of manganin may actually be regarded as a function of the temperature and that it increases by about 2×10^{-2} of itself for each degree the temperature rises at 0—70°C.[6] Hence, the manganin gauge in the present work was maintained near 30°C for over a year for ease in controlling; the resistance of manganin was thus relatively less sensitive to the temperature change, because the temperature coefficient of manganin becomes zero in the vicinity of room temperature.[6,7] The connection between the pressure vessel and the manganin gauge was made through a junction of stainless steel tubing 1/8 inch in outer diameter and 0.024 inch in inner diameter in order to make the volume of the unthermostatted part as small as possible. During the measurement of the reaction rate, their components were isolated from the Bourdon gauge and the pressure pump by shutting a valve, as is shown in Fig. 1. Pressure was directly applied by means of the pressure pump and was measured with an accuracy of 7 atm by means of a Heise Bourdon gauge, which was calibrated up to 1400 atm from time to time against a pressure balance made by the American Instrument Co., Inc. The resistance change of the gauge coil caused by the pressure change in the closed system was measured by means of the "fixed-bridge" method.[5,6] The arrangement is shown schematically in Fig. 2, in which R_1 and R_2 represent the active and the compensating coils respectively; these coils are mounted in the gauge cell. R_3 and R_4 are both precise resistance coils of 100±~1 ohm. A constant current through the bridge was supplied by a Takasago model GPO 50-2 DC power supply and was finely adjusted. The unbalanced e.m.f. was measured to 0.1 μV by means of a Yokogawa model P-7 potentiometer.

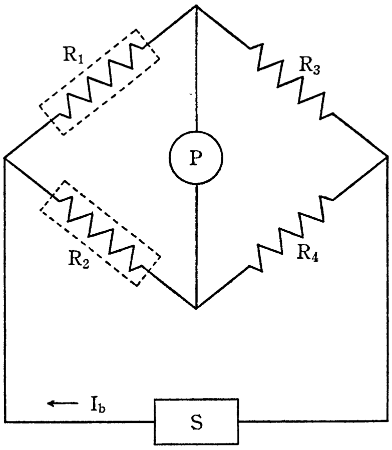

Fig. 2. The "fixed bridge" arrangement. P: Potentiometer, S: DC power supply.

Fundamentals of Measurement

In the bridge arranged as in Fig. 2, the resistance change, ΔR, with the pressure, P, of the gauge coil,

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[7] H. E. Darling and D. H. Newhall, *Trans. Amer. Soc. Mech. Engrs.*, **75**, 311 (1953).

R_1, generates across the bridge at a constant current, I_b, an unbalanced e.m.f., E_p, expressed by:

$$E_p = \frac{(R_1 \cdot R_4 - R_2 \cdot R_3 + R_4 \cdot \Delta R) I_b}{R_1 + R_2 + R_3 + R_4 + \Delta R} . \tag{1}$$

Assuming that the pressure coefficient, α, of the gauge coil has no appreciable change over the whole range of applied pressures, ΔR at a constant temperature is given by:

$$\Delta R = \alpha \cdot R_1 \cdot P . \tag{2}$$

Since the ΔR for the coil used of 120 ohm, as estimated from Eq. (2), is only a few ohm even at 10000 atm, and since it is negligible as compared with the other terms in the denominator on the right hand side of Eq. (1), one can convert Eq. (1) to a relation linear with respect to the pressure by using Eq. (2); that is,

$$E_p = E_1 + \frac{\alpha \cdot R_1 \cdot R_4 \cdot I_b \cdot P}{R_1 + R_2 + R_3 + R_4} , \tag{3}$$

where E_1 denotes an unbalanced e.m.f. that will develop when $R_1 \cdot R_4 \neq R_2 \cdot R_3$ at atmospheric pressure, E_1 being given by:

$$E_1 = \frac{(R_1 \cdot R_4 - R_2 \cdot R_3) I_b}{R_1 + R_2 + R_3 + R_4} . \tag{4}$$

Thus, it follows that E_p is proportional to only the pressure acting on the gauge coil at a constant bridge current. This suggests that one can follow the reaction with any pressure change under given conditions by measuring the unbalanced e.m.f. instead of the pressure itself. Substituting the numerical value for each term and the one used, 20.00 mA, for I_b into Eq. (3), and assuming that $R_1 \cdot R_4 = R_2 \cdot R_3$, the following equation is obtained as an approximately calculated one:

$$E_p = 1.334 \times 10^{-3} \cdot P , \tag{5}$$

where E_p is given in mV, and P, in atm. To verify Eq. (5), blank experiments when the pressure vessel entirely filled with the pressure fluid and the gauge cell were controlled at 35.00°C and 29.10°C respectively were carried out at pressures up to 2000 atm. Pressures up to 1250 atm were directly measured with an accuracy of about 0.07 atm by means of a pressure balance, and the higher pressures by means of a calibrated Bourdon gauge; the e.m.f. values were determined by averaging those obtained at increasing and decreasing pressures. The results are shown, together with the calculated line given by Eq. (5), in Fig. 3, in which the increment, $E_p - E_1$, dependent on the pressure is conveniently plotted for purposes of comparison. They are almost exactly proportional to the measured pressure of the system, as is expected from Eq. (3). The most reasonable relationship between the unbalanced e.m.f. and the pressure was obtained from the observed data using the method of least squares; it was expressed by:

$$E_p = 0.0139 + 1.320 \times 10^{-3} \cdot P \text{ mV} , \tag{6}$$

The standard deviation from this relationship was found to be 0.0125. The difference in the pressure dependence from Eq. (5) is about 1 per cent; it is not surprising and is, in fact, quite satisfactory considering that E_1 has a small definite value, as is shown in Eq. (6), because there is a small unbalance ($R_1 \cdot R_4 \neq R_2 \cdot R_3$) between the inherent values of the four resistances at atmospheric pressure. If one assumes that all the resistances have approximately the same extent of error, from which the above difference arises entirely, then the error may be estimated to be ±0.002 ohm at the most. This value is obviously within the error allowed for their resistances. Otherwise, an uncertainty involved in the pressure coefficient of the gauge coil used must also be considered, but perhaps such a small difference between the pressure dependences of the e.m.f. is predominantly due to the former cause rather than to the latter.

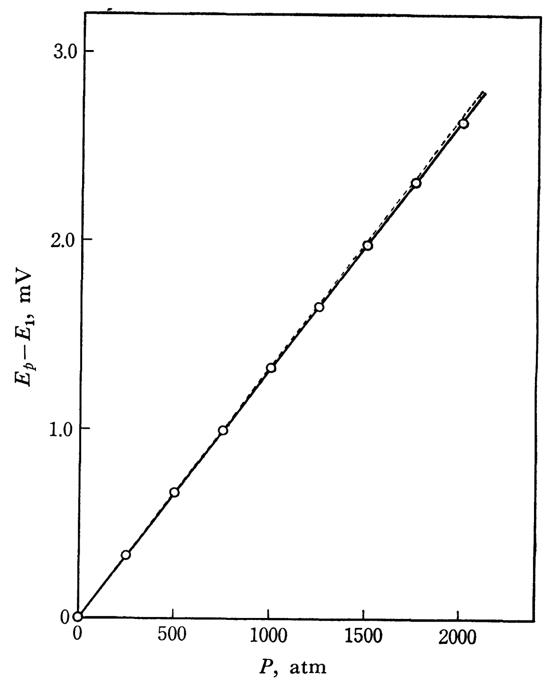

Fig. 3. Relationship between unbalanced e.m.f. and pressure.
Full line: Experimental one.
Dashed line: Calculated one.

The linearity of the manganin pressure gauge has been well verified from these results; hence, of course, it may undoubtedly be regarded as being established more exactly in a small range of pressure changes (usually below 100 atm) during the actual measurement of the reaction. The potentiometer employed in the present work can be easily read to 0.1 μV, so it is possible to measure the pressure change to 0.08 atm, at least over the pressure range up to a few thousand atmospheres, as was predicted from Eq. (6). Therefore, it is evident that one can determine the reaction rate with a reasonable accuracy by following the e.m.f. change consequent on the pressure change with the progress of the reaction in a closed system.

If a much greater sensitivity is desired in the measurement of the pressure, it may be convenient to place, on opposite sides of the bridge, two gauge coils exposed to the same pressure. When the coils, R_1 and R_4, in the arrangement shown in Fig. 2 are made up of the same material and are both equally subjected to the pressure being measured, one obtains the following approximate equation instead of Eq. (3):

$$E_p = E_1 + \frac{(\alpha_1+\alpha_4)R_1 \cdot R_4 \cdot I_b \cdot P}{R_1+R_2+R_3+R_4}, \tag{7}$$

where α_1 and α_4 are the pressure coefficients of the active coils, R_1 and R_4, respectively. Further, if their coefficients can be taken to be approximately equal to α, then it may be represented by:

$$E_p = E_1 + \frac{2\alpha R_1 \cdot R_4 \cdot I_b \cdot P}{R_1+R_2+R_3+R_4}. \tag{8}$$

Therefore, it follows that the sensitivity in the measurement can be enhanced to 2 times that in the present case when one active coil is used, as is clear from a comparison with Eq. (3).

In the practical measurement of the pressure, it is also necessary to take into account the effect due to the heat of reaction. If the heat evolved by the reaction could not be transferred to the surroundings, the reverse of when it is absorbed, fast enough to retain the isothermal condition, then the temperature of the reaction mixture varies; therefore, the crresponding pressure change must lead to a significant error in the measurement of the reaction rate. Although a theoretical analysis of the thermal effect has been pronounced by Withey and Whalley,[3] it is difficult in general to estimate to what extent the rate constant may be affected because there is no available information on the heat transfer between the reaction mixture and the thermostat in the system concerned. Because such an undesirable effect is essentially dependent upon the amount of conversion in a unit of time under given conditions, it can be experimentally eliminated by seeing whether or not the actually measured rate constants are appreciably affected by varying the concentrations of the reactant and the catalyst or the volume of the reaction mixture, *etc.*

Operation and Determination of the Rate

The reaction mixture, after being prepared, was readily preheated to a temperature somewhat higher than that of the thermostat in order to remove some dissolved air; then it was quietly poured into a glass syringe, from which air had been carefully expelled before it was stoppered with a Teflon plug. The syringe was put into the pressure vessel immersed in the thermostat, and then the vessel was quickly assembled and brought up to the desired pressure by means of the pressure pump. After about 40 min had been allowed for thermal equilibrium and the pressure had been finely adjusted to the required value on the Bourdon gauge, the valve was shut; then the unbalanced e.m.f. across the bridge, through which a constant current was passed, was potentiometrically measured at suitable time intervals. In all runs, an interval of about 2 half-lives of the reaction was taken between the first measuring set and the second one; thus, the obtained e.m.f. data were conveniently analyzed according to the Guggenheim equation:[8]

$$k_1 t + \ln(E_{t+\Delta t} - E_t) = \ln[(E_\infty - E_0)(1 - e^{-k_1 \Delta t})] = \text{constant}, \tag{9}$$

where E's are the observed e.m.f.'s, t is the reaction time and Δt is the time interval. The subscripts 0 and ∞ refer to the start and the equilibrium for reaction respectively. From Eq. (9), the first-order rate constants, k_1, were graphically obtained by plotting $\log(E_{t+\Delta t} - E_t)$ against t. The second-order rate constants, k_a, were calculated by dividing the first-order constants by the concentration of the catalyst used.

Results and Discussion

In order to test the usefulness of this apparatus in the measurement of the reaction rate, two kinds of reactions were chosen. One was the acid-catalyzed inversion of sucrose with a contraction of the volume, and the other was the base-catalyzed decomposition

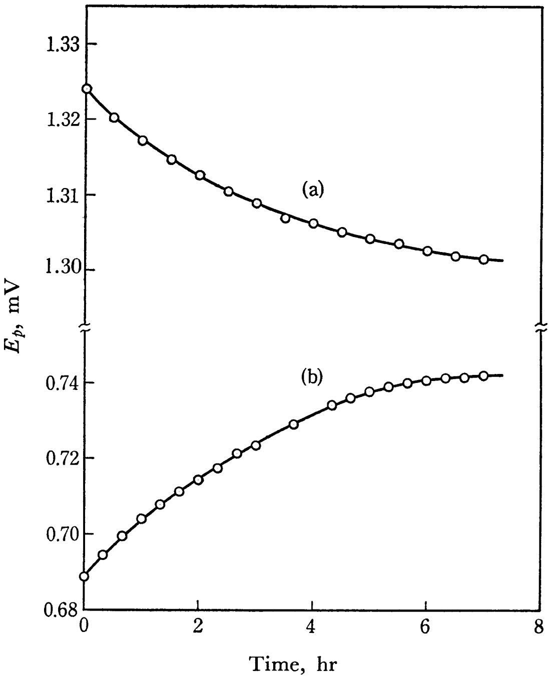

Fig. 4. Plots of E_p against time.
(a): Inversion of sucrose at 25.00°C and 1000 atm.
(d): Decomposition of diacetone alcohol at 30.00°C and 500 atm.

Table 1. Rate constants for the acid-catalyzed inversion of sucrose in water at 25.00°C

P, atm	C_{HCL}[a], mol·l^{-1}	$10^5 \times k_1$, sec^{-1}	$10^4 \times k_a$, l·mol^{-1} sec^{-1}
1[b]	0.3134	4.01	1.28
100	0.6127	7.69	1.26
500	0.7829	8.96	1.14
1000	0.8263	8.15	0.986
1500	0.4395	3.86	0.878

a) The concentration of acid denotes the value corrected for compression of the solution by using Bridgman's data[9] for water.
b) The result at 1 atm was obtained from usual dilatometric measurement.

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8) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

9) P. W. Bridgman, *Proc. Amer. Acad. Arts Sci.*, **48**, 309 (1912).

of diacetone alcohol with, on the contrary, an expansion of the volume.

First, the inversion of sucrose was measured at 25.00°C in aqueous dilute hydrochloric acid which contained initially about 0.5 mol/l of the reactant; here, the total pressure change during the kinetic measurements was in the range of from 9 to 20 atm. A typical curve obtained is shown in Fig. 4, while its Guggenheim plot is shown in Fig. 5. The first-order rate constants, as calculated from similar plots obtained at various pressures, are listed in Table 1, together with the second-order constants.

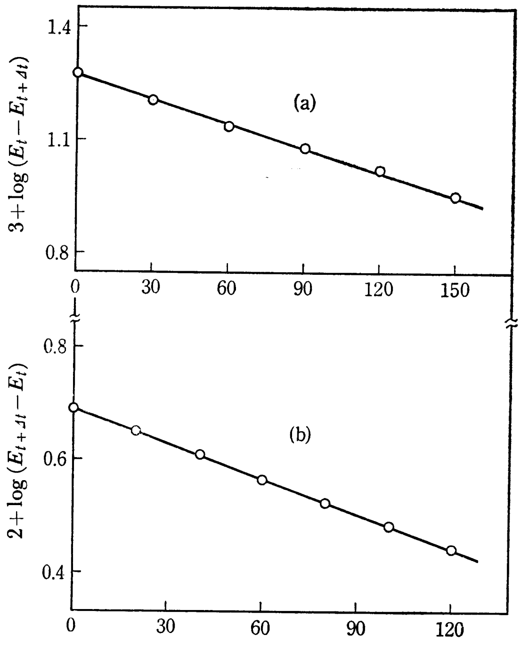

Fig. 5. Guggenheim plots for two e.m.f. data.
(a): Inversion of sucrose.
(b): Decomposition of diacetone alcohol.

The second-order rate constants as a function of the pressure are graphically shown in Fig. 6, together with those calculated from the data of Cohen and de Boer,[10] which were obtained by measurement with a polarimeter. The piezometrically-determined values are less than these by about 15 to 21 per cent, but it is not determined whether such a discrepanct results from the differences in the method of measurement or in the concentration of the acid used (their reaction mixtures were 0.0625 N in hydrochloric acid), or from other causes. The volumes of activation, $\Delta V^{\ne}$, were calculated from the slopes at 1 atm using the usual equation:

$$\left(\frac{\partial \ln k_a}{\partial T}\right)_T = -\frac{\Delta V^{\ne}}{RT}, \qquad (10)$$

where $\boldsymbol{R}$ is the gas constant and T is the absolute temperature. The value determined from the observed data is 6.0 cm^3/mol; this is in good agreement with the 5.0 cm^3/mol value from the data of Cohen

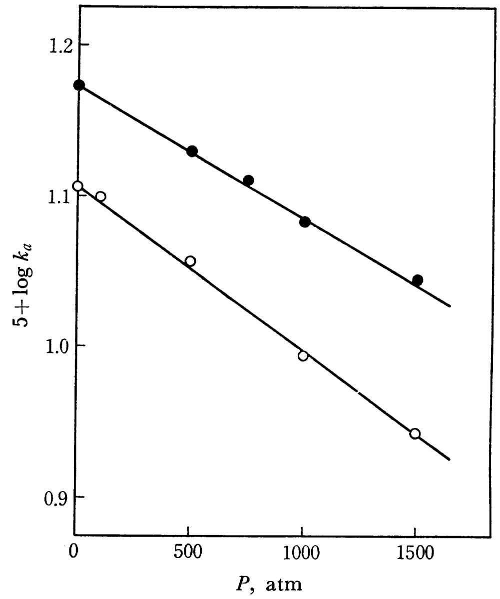

Fig. 6. Effect of pressure on the acid-catalyzed inversion of sucrose in water at 25.00°C.
●: Cohen and de Boer,[10] ○: This work.

and de Boer and also with the 6.0±∼0.3 cm^3/mol obtained by Whalley[11] from the same data.

The decomposition of diacetone alcohol as another reaction was measured in an aqueous solution involving initially about 0.4 mol/kg of the reactant and an appropriate amount of sodium hydroxide as a catalyst at 30.00°C and at various pressures. There was a pressure change of from 14 to 40 atm during the kinetic measurements. The results for this reaction are shown, along with those of sucrose, in Figs. 4 and 5. For purposes of comparison, the rates of the same reaction were also measured separately using an analytical method based on the oximation of the carbonyl group with hydroxylamine hydrochloride.[12] Both

TABLE 2. RATE CONSTANTS FOR THE BASE-CATALYZED DECOMPOSITION OF DIACETONE ALCOHOL IN WATER AT 30.00°C[a)]

P, atm	method[b)]	$10^3 \times C_{\mathrm{NaOH}}$ mol·kg^{-1}	$10^4 \times k_1$ sec^{-1}	$10^2 \times k_a$, kg·mol^{-1}sec^{-1}
1	a	7.222	1.08	1.50
1	b	7.920	1.19	1.50
100	c	11.57	1.79	1.55
500	a	7.181	1.24	1.73
500	c	4.657	0.797	1.71
1000	a	6.173	1.19	1.93
1000	c	8.667	1.71	1.97
1500	a	6.173	1.30	2.11
1500	c	7.753	1.71	2.21

a) The measurements with analytical method were made in a thermostat controlled to within ±0.05°C.
b) a: analytical method, b: usual dilatometric method, c: piezometric method.

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[10] E. Cohen and R. B. de Boer, *Z. Phys. Chem.* (Leipzig), **84**, 41 (1913).

[11] E. Whalley, *Trans. Faraday Soc.*, **55**, 798 (1959).

[12] D. M. Smith and J. Mitchell, Jr., *Anal. Chem.*, **22**, 750 (1950).

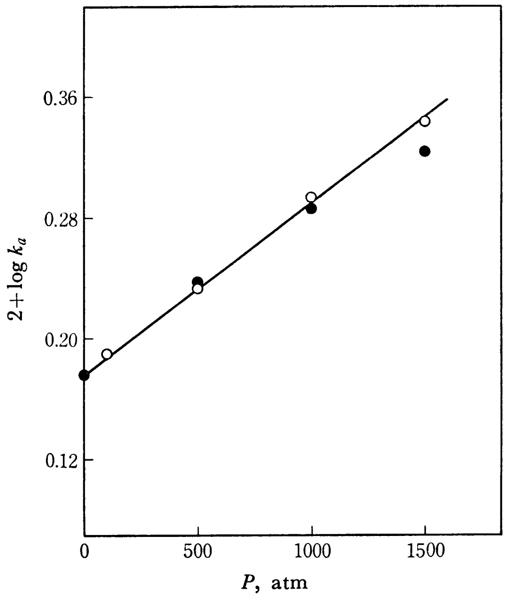

Fig. 7. Effect of pressure on the base-catalyzed decomposition of diacetone alcohol in water at 30.00°C.
●: Analytical method, ○: Piezometric method.

rate constants obtained are listed in Table 2; the agreement between them is very satisfactory. The volume of activation obtained from Fig. 7 was almost the same, -6.6 cm^3/ mol, in both cases, and no appreciable difference could be found graphically. The mechanistic consideration of the observed value of $\Delta V^{\neq}$ for this reaction has not been made here, for it is beyond the present purposes, but it will be reported elsewhere. In addition, the rate of the depolymerization of paraldehyde catalyzed by 0.0991 mol/l perchloric acid was found in the same way to be 7.36×10^{-4} l/mol·sec at 35.00°C and 500 atm; this is in good agreement with the 7.12×10^{-4} l/mol·sec obtained by the piezometric measurements of Withey and Whalley.[4)]

From some preliminary measurements for each reaction, it might be presumed that all of the results mentioned above were not significantly affected by the heat of reaction during the measurements.

Consequently, it may be concluded that the apparatus and the technique employed in the present work are sufficiently applicable to the rate measurements of any other reaction with a change in volume.

The author should like to thank Mr. H. Ōto for his help in the construction of the high-pressure apparatus and Mr. J. Ōtsubo for his help in the kinetic measurements.