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THE MECHANISM OF THE DECOMPOSITION OF CHLOROFORM

By

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Since LIEBIG¹⁾ showed in 1832 that chloroform decomposes in aqueous potassium hydroxide, the reaction has been investigated by a number of authors²⁾³⁾ in aqueous and alcoholic alkaline solution and the end products were confirmed to be carbon monoxide, formate and hydrogen chloride. GEUTHER²⁾ among them suggested on the basis of these results that chloroform was of configuration $\text{CCl}_2\cdot\text{HCl}$ and hydrogen chloride removed by alkali to give carbon dichloride, which in turn hydrolysed to carbon monoxide or formate.

HORIUTI and SAKAMOTO have later found that hydrogen is exchanged between chloroform and aqueous solution rapidly in comparison with decomposition.⁴⁾

The present authors have now observed the decomposition rate at 100°C at different pH and neutral salt concentrations. The mechanism of decomposition was deduced from the results of the experiment incorporated with those of chlorine exchange between chloroform and solution reported in the foregoing paper⁵⁾ and of the recent observation of hydrogen exchange by KANEKO and SATO⁶⁾ under similar conditions.

§ 1. Experimental Procedure

One or 1.5 cc chloroform was sealed air-free together with 5 cc to 10 cc aqueous solution of known pH with or without addition of neutral salt or solid hydroxides in a quartz tube of 23~28 cc capacity, shaken briskly at 100°C for a recorded time, the quartz tube opened, about 5 cc solution pipetted out and analysed for the decomposition rate at different pH in several different ways as below.

(i) The pH of the sample was determined at room temperature by means of BECKMAN pH meter or of pH indicator. The amount of decomposition and pH at 100°C were worked out from the results as

described in § 2 for different contact time and thereafter the rate at different pH values was determined.

(ii) The rate was determined as described in § 2 by measuring the amount of liberated chloride ion by titration of MOHR'S or VOLHARD'S method or by colorimetry according to UTSUMI⁷⁾ of ferric thiocyanate liberated by chloride ion in the presence of mercury thiocyanate and iron alum. The associated pH-change at 100°C was determined either (ii. a) by calculating it from known solubilities of solid hydroxides present or (ii. b) by pH measurement at room temperature by means of BECKMAN pH meter or of titration with standard oxalic acid solution as detailed in § 2.

Chloroform sample was the preparation as that used in the previous experiment.⁸⁾

Solution of different pH used was simply distilled water or the latter to which was added a proper quantity of aqueous sodium hydroxide or sulfuric acid or solid hydroxides Ca(OH)₂ and Mg(OH)₂, for retarding pH-shift due to decomposition. Neutral salt added was sodium chloride or sodium sulfate.

§ 2. Decomposition Rate at Different pH

Admitting that a chloroform molecule yields, as it decomposes, three chloride ions, the decomposition rate V_a reckoned to unit volume of solution is expressed as,

$$V_a = \frac{1}{3} \frac{d\Delta[\text{Cl}^-]}{dt} \quad (2.1)$$

where $\Delta[\text{Cl}^-]$ is the increment of chloride ion concentration $[\text{Cl}^-]$ in solution due to decomposition and t the time of contact.

In the case of (ii) in the foregoing section when $[\text{Cl}^-]$ was directly observed, $d\Delta[\text{Cl}^-]/dt$ was determined simply as the quotient of $\Delta[\text{Cl}^-]$ over t ; associated range of pH at 100°C in the respective case of (ii. a) or (ii. b) was calculated, as described below respectively under the same heading from the known solubilities of solid hydroxides or from pH at room temperature.

In the other case (i), when pH alone was measured, $[\text{Cl}^-]$ and hence V_a was determined indirectly as described under heading (i), neglecting the formate evolution by decomposition; this neglect is confirmed valid by the result of (ii. b) as shown in § 3.

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(i) We have because of electric neutrality of the solution,

$$\Delta[\text{Cl}^-] + [\text{OH}^-] = [\text{H}^+] + \text{I} \quad (2.2)$$

where $[\text{OH}^-]$ or $[\text{H}^+]$ is normal concentration of hydroxide or hydrogen ion respectively and I the excess of total concentration of cation over that of anion, exclusive of $[\text{H}^+]$, $[\text{OH}^-]$ and $\Delta[\text{Cl}^-]$; I is identified, for instance, assuming the complete dissociation, with the concentration of sodium ion for the sodium hydroxide solution or with negative value of sulfate ion concentration (in normal) for the solution acidified by sulfuric acid, irrespective of neutral salt added which contributes nothing to I. The I is taken to remain constant during the progress of decomposition in the case of (i) when definite amount of strong electrolytes alone is present in solution.*) Rewriting $[\text{OH}^-]$ or $[\text{H}^+]$ in (2.2) into respective ratio of activity a^{OH^-} or a^{H^+} to activity coefficient f^{OH^-} or f^{H^+} and introducing the thermodynamical dissociation constant,

$$K_h = a^{\text{H}^+} a^{\text{OH}^-} \quad (2.3)$$

we have,

$$\frac{K_h}{a^{\text{H}^+} f^{\text{OH}^-}} - \frac{a^{\text{H}^+}}{f^{\text{H}^+}} = \text{I} - \Delta[\text{Cl}^-] \quad (2.4)$$

or before contact in particular,

$$\frac{K_h}{a^{\text{H}^+} f^{\text{OH}^-}} - \frac{a^{\text{H}^+}}{f^{\text{H}^+}} = \text{I} \quad (2.5)$$

The I was determined from pH-observation at room temperature by successive approximation as below; it was first calculated from the observed pH or a^{H^+} by putting $f^{\text{H}^+} = f^{\text{OH}^-} = 1$ in (2.5) and in K_h in it the values at different room temperatures given in the Table;

Temperature °C	12	15	18	20	25
$K_h \times 10^{-14}$	0.35 ***)	0.46 ***)	0.59 **)	0.7 ***)	1.04 **)

appropriate ionic strength μ was now worked out from the value of I incorporated with known concentration of neutral salt, if any, equating a^{H^+} or K_h/a^{H^+} respectively to $[\text{H}^+]$ or $[\text{OH}^-]$; the f^{H^+} and f^{OH^-} were now computed according to the limiting law,

$$-\log_{10} f^{\text{H}^+} = -\log_{10} f^{\text{OH}^-} = \frac{1.8148 \times 10^{-6}}{(DT)^{3/2}} \sqrt{\mu} \quad (2.6)$$

where T is absolute temperature, D the dielectric constant, calculated according to the empirical formula of DRUDE,⁹⁾

$$D = 88.23 - 0.4044 t + 0.001035 t^2$$

*) If formate were evolved by decomposition, I would include the negative value of formate ion concentration in alkaline region, whereas none of it in acidic one because of its weak dissociation, so that I would increase as the solution shifts from alkaline to acidic region along with the progress of decomposition.

**) HEYDWEILLER, Landolt-Börnstein Tabellen II. p. 1164.

***) Interpolated from the values observed by HEYDWEILLER.

Using the value of f^{H^+} or f^{OH^-} thus obtained, I and henceforth μ were computed again according to (2.5), equating $\alpha^{\text{H}^+}/f^{\text{H}^+}$ or $K_h/\alpha^{\text{H}^+}f^{\text{OH}^-}$ now to $[\text{H}^+]$ or $[\text{OH}^-]$ respectively. This procedure of successive approximation was repeated until I-value remained practically unvaried by the repetition.

The difference $\text{I}-\Delta[\text{Cl}^-]$ after contact was worked out from α^{H^+} , observed then at room temperature, putting first $f^{\text{H}^+} = f^{\text{OH}^-} = 1$ as above; $\Delta[\text{Cl}^-]$ was determined from the approximate value of $\text{I}-\Delta[\text{Cl}^-]$ thus obtained and the final value of I obtained above, and included in the calculation of μ . Successive approximation was then carried out quite similarly otherwise.

The $\text{I}-\Delta[\text{Cl}^-]$ -value at 100°C was obtained by multiplying that at room temperature obtained above by the ratio $\alpha = 0.96$ of the specific volume of water at room temperature to that at 100°C . The $d\Delta[\text{Cl}^-]/dt$ and henceforth V_d of (2.1) were now calculated from $\text{I}-\Delta[\text{Cl}^-]$ at 100°C according to the identity,

$$\frac{d\Delta[\text{Cl}^-]}{dt} = \frac{d(\Delta[\text{Cl}^-]-\text{I})}{dt} = \frac{d \log |\Delta[\text{Cl}^-]-\text{I}|}{d \log t} \cdot \frac{\Delta[\text{Cl}^-]-\text{I}}{t}$$

taking advantage of the constancy of I and the greater relative rate of variation of $\Delta[\text{Cl}^-]-\text{I}$ compared with that of $\Delta[\text{Cl}^-]$.

The pH of solution at 100°C was now determined by solving quadratic equation (2.4) with respect to α^{H^+} , putting into it $K_h = 48 \times 10^{-14}$ *) and $\text{I}-\Delta[\text{Cl}^-]$ obtained above at 100°C and $f^{\text{H}^+} = f^{\text{OH}^-}$ -value at 100°C calculated by (2.6) on the basis of μ obtained above multiplied by α .

(ii. a) We have in this case for I of (2.4),

$$\text{I} = [\text{Me}^{++}] = \alpha^{\text{Me}^{++}}/f^{\text{Me}^{++}} \quad (2.7)$$

by definition assuming the complete dissociation of hydroxide into bivalent metallic ion and hydroxide ion. Hence we have by (2.4),

$$\frac{K_h}{\alpha^{\text{H}^+}f^{\text{OH}^-}} - \frac{\alpha^{\text{H}^+}}{f^{\text{H}^+}} = [\text{Me}^{++}] - \Delta[\text{Cl}^-] = \frac{\alpha^{\text{Me}^{++}}}{f^{\text{Me}^{++}}} - \Delta[\text{Cl}^-] \quad (2.8)$$

The pH or α^{H^+} before contact is calculated by (2.8) putting $\Delta[\text{Cl}^-] = 0$ in it, equating $[\text{Me}^{++}]$ to the known concentration C of the saturated solution, neglecting perhaps safely $\alpha^{\text{H}^+}/f^{\text{H}^+}$ -term and working out $f^{\text{H}^+} = f^{\text{OH}^-}$ by (2.6) on the basis of C .

In this case activity product,

$$\alpha^{\text{Me}^{++}} (\alpha^{\text{OH}^-})^2 = S \quad (2.9)$$

is kept constant instead of I or $[\text{Me}^{++}]$ due to the presence of solid phase. The S is calculated from the above value of α^{H^+} , K_h given before and $f^{\text{Me}^{++}}$ worked out similarly as f^{OH^-} by the limiting value, writing (2.9) according to (2.3) as,

$$S = f^{\text{Me}^{++}} [\text{Me}^{++}] \cdot \left(\frac{K_h}{\alpha^{\text{H}^+}} \right)^2$$

The pH at 100°C after contact is now calculated for known value of $\Delta[\text{Cl}^-]$ by successive approximation as follows. We have by (2.8) and (2.9),

$$\frac{K_h}{\alpha^{\text{H}^+}f^{\text{OH}^-}} - \frac{\alpha^{\text{H}^+}}{f^{\text{H}^+}} = \frac{S(\alpha^{\text{H}^+})^2}{f^{\text{Me}^{++}}K_h^2} - \Delta[\text{Cl}^-] \quad (2.10)$$

*) NOYES and KATO, Landolt-Börnstein Tabellen II. p. 1164.

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Putting first in (2.10) those values of f^{H^+} , f^{OH^-} and $f^{\text{Me}^{++}}$ obtained above for $\Delta[\text{Cl}^-]=0$, α^{H^+} and hence α^{OH^-} and $\alpha^{\text{Me}^{++}}$ are determined by (2.3) and (2.9). The concentrations $[\text{Me}^{++}] = \alpha^{\text{Me}^{++}}/f^{\text{Me}^{++}}$ etc. are computed using the above values of $f^{\text{Me}^{++}}$ etc. and, from these concentrations and the given $\Delta[\text{Cl}^-]$, the ionic strength is now determined; activity coefficients are recalculated by the new value of ionic strength and thereafter the above calculation is repeated until α^{H^+} varies practically no more.

(ii. b) The I at 100°C is calculated from pH before contact similarly as in the case of (i) by (2.5). The $I - \Delta[\text{Cl}^-]$ at 100°C is now determined as the difference between the I at 100°C thus determined and $\Delta[\text{Cl}^-]$ directly observed by titration or by colorimetry multiplied by α , from which α^{H^+} or pH at 100°C worked out similarly as in the case of (i). In the case of highest concentration of alkali (ca. 4 N. of runs 1 and 2, Table 3) when the ionic strength of alkali was determined by titration, pH was not calculated allowing for the ionic interaction because of expected unreliability but given conventionally as the classical value or the quotient of K_b over the titrated concentration of alkali.

It might be expected from (2.4) that the rate of variation of $\Delta[\text{Cl}^-]$ and hence V_a are upper bounds to the respective actual values, inasmuch as the limiting law (2.6) gives the lower bounds to the activity coefficient, neglecting its variation with pH, and on the other hand that V_a calculated classically putting $f^{\text{H}^+} = f^{\text{OH}^-} = 1$ gives a lower bound to the actual value, admitting that f^{H^+} or f^{OH^-} does not exceed unity at moderate ionic strength. The two values might hence indicate the range within which the actual one lies.

§ 3. Experimental results

Table 1 or 2 shows the results of decomposition followed by method (i) of §1 by means of BECKMAN pH meter and pH indicator either with or without addition of neutral salt respectively. Each series in the Tables includes several parallel runs initiated with the same quantities of chloroform, aqueous solution and of the same addition shown respectively in the second to the fourth columns in either Table but of different time of contact shown in the fifth column, where zero of time in particular corresponds to the initial condition.

Next columns give pH at 100°C calculated according to §2 from values at room temperature given in parenthesis and the room temperature of observation. The last column shows $I - \Delta[\text{Cl}^-]$ in normal at 100°C computed according to §2 from data in the foregoing columns; $I - \Delta[\text{Cl}^-]$ at $t=0$ is I itself. The pH observed by BECKMAN pH meter was preferred in the above calculation to that by indicator when the both were available.

TABLE 1 Decomposition of Chloroform in Aqueous Solution at 100°C Followed by BECKMAN pH Meter and pH Indicator. Neutral Salt Absent.

Series	Quantity of		Additions	Time of Contact min.	pH		Room Temp.	I-4[Cl ⁻] N
	Chloro- form cc. at Room Temp.	Aqueous Solution cc. at Room Temp.			Beckman pH Meter	pH Indicator		
1	1	10	None	0	6.11 (6.68)	—	25	-1.53×10^{-7}
	"	"		9	5.76 (5.82)	—	"	-1.44×10^{-6}
	"	"		29	5.13 (5.13)	—	"	-7.12×10^{-6}
	"	"		59	3.88 (3.88)	—	"	-1.27×10^{-4}
2	1	10	NaOH	0	10.07 (11.75)	—	25	6.31×10^{-3}
	"	"		0.25	9.76 (11.45)	—	"	3.09×10^{-3}
	"	"		0.50	8.36 (10.05)	—	"	1.24×10^{-4}
	"	"		1	6.58 (8.20)	—	"	1.80×10^{-6}
3	1	10	H ₂ SO ₄	0	2.11 (2.08)	2.08 (2.05)	18	-9.18×10^{-3}
	"	"		256	2.11 (2.08)	2.05 (2.02)	19	-9.18×10^{-3}
	"	"		2420	1.96 (1.93)	1.88 (1.85)	"	-1.32×10^{-2}
	"	"		9430	1.73 (1.70)	1.63 (1.60)	"	-2.32×10^{-2}
	"	"		17240	—	1.43 (1.40)	"	-4.83×10^{-2}
4	1	10	NaOH	0	6.26 (7.75)	—	19	3.33×10^{-7}
	"	"		1	6.14 (6.95)	—	"	-5.19×10^{-8}
	"	"		9	5.65 (5.65)	—	"	-2.15×10^{-6}
	"	"		60	4.27 (4.27)	—	"	-5.16×10^{-5}

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Series	Quantity of		Additions	Time of Contact min.	pH		Room Temp.	I - A [Cl ⁻] N
	Chloroform cc. at Room Temp.	Aqueous Solution cc. at Room Temp.			Beckman pH Meter	pH Indicator		
5	1	10	H ₂ SO ₄	0	4.30 (4.30)	—	14	-4.82 × 10 ⁻⁵
	"	"		17	3.83 (3.83)	—	"	-1.42 × 10 ⁻⁴
	"	"		240	3.12 (3.12)	—	"	-7.28 × 10 ⁻⁴
	"	"		1740	2.50 (2.50)	—	"	-3.04 × 10 ⁻³
6	1	10	NaOH	0	10.81 (12.95)	—	12	4.37 × 10 ⁻²
	"	"		0.42	10.32 (12.50)	—	"	1.50 × 10 ⁻²
	"	"		0.83	8.48 (10.65)	—	"	2.11 × 10 ⁻⁴
	"	"		2	6.59 (8.70)	—	"	2.37 × 10 ⁻⁶
	"	"		11	6.11 (6.70)	—	"	-2.46 × 10 ⁻⁷
7	1.5	10	H ₂ SO ₄	0	—	4.10 (4.10)	18	-7.63 × 10 ⁻⁵
	"	"		20	—	3.70 (3.70)	"	-1.92 × 10 ⁻⁴
	"	"		60	—	3.55 (3.55)	"	-2.71 × 10 ⁻⁴
	"	"		270	—	3.10 (3.10)	"	-7.63 × 10 ⁻⁴
	"	"		1070	—	2.85 (2.85)	17	-1.35 × 10 ⁻³
	"	"		2990	—	2.25 (2.25)	"	-5.40 × 10 ⁻³
8	1.5	10	H ₂ SO ₄	0	—	4.10 (4.10)	20	-7.63 × 10 ⁻⁵
	"	"		60	—	3.55 (3.55)	"	-2.71 × 10 ⁻⁴
	"	"		1200	—	2.70 (2.70)	17	-1.92 × 10 ⁻³
9	1.5	10	NaOH	0	8.49 (10.33)	—	20	1.44 × 10 ⁻⁴
	"	"		0.25	7.65 (9.50)	—	"	2.12 × 10 ⁻⁵

Series	Quantity of		Additions	Time of Contact min.	pH		Room Temp.	I-4[Cl ⁻] N
	Chloroform cc. at Room Temp.	Aqueous Solution cc. at Room Temp.			Beckman pH Meter	pH Indicator		
	1.5	10		0.61	6.86 (8.70)	—	20	3.37×10^{-6}
	"	"		1	6.41 (8.10)	—	"	8.37×10^{-7}
10	1.5	5	NaOH	0	7.50 (9.35)	—	20	1.50×10^{-5}
	"	"		0.50	7.25 (9.10)	—	"	8.45×10^{-6}
	"	"		0.76	6.55 (8.33)	—	"	1.43×10^{-6}
	"	"		1	6.34 (7.96)	—	"	6.02×10^{-7}
	"	"		2.5	6.05 (6.40)	—	"	-3.65×10^{-7}

TABLE 2 Decomposition of Chloroform in Aqueous Solution at 100°C Followed by BECKMAN pH Meter and pH Indicator. Neutral Salt Present.

Series	Quantity of		Additions	Time of Contact min.	pH		Room Temp.	I-4[Cl ⁻] N
	Chloroform cc. at Room Temp.	Aqueous Solution cc. at Room Temp.			Beckman pH Meter	pH Indicator		
1	1.5	10	H ₂ SO ₄ + 0.354 N NaCl	0	—	4.21 (4.15)	18	-1.35×10^{-4}
	"	"		20	—	4.16 (4.10)	"	-1.51×10^{-4}
	"	"		60	—	4.01 (3.95)	"	-2.13×10^{-4}
	"	"		270	—	3.51 (3.45)	"	-6.75×10^{-4}
	"	"		1200	—	2.96 (2.90)	"	-2.39×10^{-3}
2	1	5	NaOH + 0.062 N NaCl	0	10.78 (12.57)	—	19	4.66×10^{-2}
	"	"		0.42	10.66 (12.48)	—	22	3.79×10^{-2}
	"	"		0.42	10.62 (12.50)	—	20	3.21×10^{-2}

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Series	Quantity of		Additions	Time of Contact min.	pH		Room Temp.	I- Δ [Cl ⁻] N
	Chloroform cc. at Room Temp.	Aqueous Solution cc. at Room Temp.			Beckman pH Meter	pH Indicator		
	1	5		0.84	9.48 (11.30)	—	21.5	2.32×10^{-3}
	"	"		2	6.74 (8.50)	—	22	3.87×10^{-6}
	"	"		12	6.17 (7.20)	—	21	8.02×10^{-8}
3	1	5		0	5.76 (5.81)	—	17	-1.67×10^{-6}
	"	"		9	5.51 (5.51)	—	"	-3.33×10^{-6}
	"	"	0.01 N- NaCl	25	4.72 (4.70)	—	"	-2.15×10^{-5}
	"	"		40	4.17 (4.15)	—	"	-7.63×10^{-5}
	"	"		70	3.98 (3.96)	—	"	-1.18×10^{-4}
4	1	5		0	4.14 (4.12)	—	20	-8.18×10^{-5}
	"	"		20	4.03 (4.00)	—	"	-1.08×10^{-4}
	"	"	H ₂ SO ₄ + 0.01 N- NaCl	60	3.86 (3.82)	—	"	-1.63×10^{-4}
	"	"		80	3.62 (3.60)	—	"	-2.71×10^{-4}
	"	"		270	3.27 (3.25)	—	"	-6.06×10^{-4}
5	1	5		0	4.23 (4.20)	—	14	-6.96×10^{-5}
	"	"	H ₂ SO ₄ +	20	4.03 (4.05)	—	17	-9.84×10^{-5}
	"	"	0.01 N- Na ₂ SO ₄	60	3.90 (3.87)	—	14	-1.49×10^{-4}
	"	"		270	3.40 (3.37)	—	17	-4.71×10^{-4}
6	1	5		0	5.79 (5.85)	—	20	-1.56×10^{-6}
	"	"		10	5.50 (5.50)	—	"	-3.50×10^{-6}
	"	"	0.01 N- Na ₂ SO ₄	24	4.83 (4.80)	—	"	-1.75×10^{-5}
	"	"		40	4.17 (4.13)	—	"	-7.99×10^{-5}
	"	"		80	3.95 (3.92)	—	"	-1.33×10^{-4}

TABLE 3 Decomposition of Chloroform in Aqueous Solution at 100°C
Followed by MOHR'S and VOLHARD'S Method of Titration.

Runs	Quantity of		Additions	Time of Contact min.	pH at 100 C			N/100 AgNO ₃ titer <i>w</i> cc. for 1cc. Aqueous Solution After Contact **)			Decomposition Rate $V_d = \frac{1}{3} \cdot \frac{aw}{100} \cdot \frac{1}{t}$ mol/lit. min.
	Chloroform cc. at Room Temp.	Aqueous Solution cc. at Room Temp.			Before Contact	After Contact	Method	Mohr's	Volhard's	Average	
1	0.7	4	NaOH	1	12.8 *) (14.511)	11.5 *) (13.898)	Titration	230	215	223	7.1×10^{-1}
2	"	"	"	2	12.8 *) (14.511)		Titration	270	264	267	
3	1.5	5	Sat. Ca(OH) ₂	1	10.49	10.20	Solubility	6.8		6.8	2.2×10^{-2}
4	"	"	Sat. Mg(OH) ₂	10	8.47	7.76	Solubility	0.55	0.55	0.55	1.8×10^{-4}
5	"	"	H ₂ SO ₄	6130	0.1 (0.1)	0.1 (0.1)	Beckman	0.95		0.95	5.0×10^{-7}
6	1	10	H ₂ SO ₄	256	2.11 (2.08)	2.11 (2.08)	"	0.069	0.028	0.048	6.0×10^{-7}
7	"	"	"	2420	2.11 (2.08)	1.96 (1.93)	"	0.44	0.39	0.42	5.5×10^{-7}
8	"	"	"	9430	2.11 (2.08)	1.73 (1.70)	"	1.46	1.34	1.40	4.8×10^{-7}
9	"	"	"	240	4.30 (4.30)	3.12 (3.12)	"	0.10	0.090	0.096	1.3×10^{-6}
10	"	"	"	1740	4.30 (4.30)	2.50 (2.50)	"	0.34	0.28	0.31	5.2×10^{-7}
11	"	4	H ₂ SO ₄ + 4 N NaCl	6200	(1.89)	(1.78)	"	1.1		1.1	5.7×10^{-7}
12	"	"	H ⁺ SO ₄ + 5.2 N Na ₂ SO ₄	2000	(2.00)	(1.96)	"	0.38		0.38	6.1×10^{-7}

"Titration": Determination of pH at room temperature given in parenthesis by titration with standard oxalic acid solution with phenolphthalein as indicator.

"Beckman": Determination of pH at room temperature given in parenthesis by means of Beckman pH meter.

"Solubility": Calculation of pH at 100°C from known solubility of solid hydroxides as in the foregoing paper [Ref.5].

α : Ratio of specific volume of water at room temperature to that at 100°C.

*) pH classically computed as the negative logarithm of the quotient of $K_a = 1.000 \times 10^{-14}$ at room temperature or $K_a = 48 \times 10^{-14}$ at 100°C divided by the titrated concentration of alkali or the latter multiplied by α respectively. Figures in the parentheses correspond to the accuracy of titration.

**) Corresponding titer before contact was found by both the methods less than 0.01 cc.

TABLE 4 Decomposition of Chloroform in Aqueous Solution at 100°C Followed by Colorimetric Method.

Runs	Quantity of		Additions	Time of Contact min.	pH at 100°C *)		Corresponding Concn. <i>m</i> of Standard KCl Solution**) mg KCl/lit. after Contact	Decomposition Rate $V_d = \frac{1}{3} \cdot \frac{\beta m}{35.5} \cdot \frac{1}{t} \cdot 10^{-3}$ mol/lit. min.
	Chloro- form cc. at Room Temp.	Aqueous Solution cc. at Room Temp.			Before Contact	After Contact		
1	1	5	None	10	5.5 (5.5)	5.2 (5.2)	15	6.4×10^{-7}
2	"	"	H ₂ SO ₄	"	4.1 (4.1)	3.6 (3.6)	15	6.4×10^{-6}
3	"	"	None	"	5.6 (5.6)	5.3 (5.3)	1.5	6.4×10^{-7}
4	"	"	H ₂ SO ₄	"	4.2 (4.2)	3.9 (3.9)	15	6.4×10^{-6}
5	"	"	"	"	4.6 (4.6)	4.3 (4.3)	7.5	3.2×10^{-6}

β : α of Table 3 times the fraction of Cl-weight in KCl.

*) Method of pH-determination is exclusively that of Beckman pH meter of Table 3.

**) Corresponding concentration before contact was found far less than 1 mg/lit. by the same method.

The $\log_{10} V_a$ calculated from $I - \Delta[\text{Cl}^-]$ in Table 1 or 2 according to the foregoing section is shown in Table 5 or 6 respectively against several round pH and $\log_{10} V_a$ of each series is shown in Table 5 by a full line in Fig. 1. The dotted line in the same figure shows "lower bound" of series 6 or its classical value calculated assuming $f^{\text{H}^+} = f^{\text{OH}^-} = 1$ according to §2. The latter "lower bound" lies below the appropriate full line, i.e., the "upper bound" in accordance with what was expected in the foregoing section, whereas both the "bounds" of other series fall in practically with each other locating perhaps the actual value there.

Fig. 2 shows $\log_{10} V_a$ of Table 6 observed with addition of neutral salt by a full line for each series. Dotted line there shows the average*) of $\log_{10} V_a$ without addition of neutral salt for comparison; series 6 of Table 1 was excluded from the average but shown separately by full line denoted by [6], the neutral salt formed by the neutralization of alkali amounting in the latter case to as much as 0.09N, even more than 0.062N of added neutral salt of series 2 of Table 2. Curves [6] and 2 are seen almost to fall in with each other. The curve with maximum denoted by 3 and 6 shows the coincident results of the respective series with addition of NaCl or Na_2SO_4 of the same normality.

Table 3 shows the result of decomposition followed by titration according to (ii. a) and (ii. b) in §1. Column "pH at 100°C" shows pH before or after contact and methods of its determination; they are the calculations from values at room temperature in parenthesis determined by titration with standard oxalic acid solution or by BECKMAN pH meter and the calculation from known solubilities of solid hydroxides added.

Next column shows the titer w cc of N/100 AgNO_3 solution for 1 cc sample of aqueous solution after contact by MOHR'S or VOLHARD'S method and the last column the decomposition rate calculated from averaged w multiplied by α to allow for volume expansion from room temperature to 100°C. The result is shown in Fig. 1 by circlets each at the middle of pH range, if it varied.

Table 4 gives the result of decomposition colorimetrically followed. The last two columns show concentration m in mgm KCl/litre of standard KCl solution found colorimetrically just to coincide with the chloride ion concentration of the solution after contact and the decomposition rate calculated from m multiplied by a factor

*) Average of $\log_{10} V_a$ given in Table 5 for every pH. It is hence the geometrical mean with regard to V_a .

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TABLE 5

$-\log_{10} V_a$ mol/l. min. Additions absent.

Series pH	1	2	3	4	5	6	7	8	9	10
1.4	.	.	.	6.12
1.6	.	.	.	6.19
1.8	.	.	6.39	6.21
2.0	.	.	6.25	6.06
2.2	6.18	6.18	.	.
2.4	6.25	6.25	.	.
2.6	6.22	.	6.28	6.28	.	.
2.8	6.24	.	6.32	6.32	.	.
3.0	6.18	.	6.29	6.29	.	.
3.2	6.16	.	6.28	6.28	.	.
3.4	6.20	.	6.06	6.06	.	.
3.6	6.02	.	6.07	6.07	.	.
3.8	5.88	.	5.78	5.78	.	.
3.9	5.75	.	5.62	5.62	.	.
4.0	5.54	.	.	5.69	5.73	.	5.30	5.30	.	.
4.2	5.70	.	.	5.91
4.4	5.87	.	.	6.15
4.6	6.14	.	.	6.35
4.8	6.35	.	.	6.52
5.0	6.55	.	.	6.68
5.2	6.76	.	.	6.84
5.4	7.01	.	.	6.96
5.6	7.19	.	.	7.06
5.8	7.27	.	.	7.12
6.0	7.23	.	.	7.05	7.25
6.1	7.74	.	.	.	6.85
6.2	7.22	.	.	.	6.44
6.3	6.86	.	.	.	6.26
6.4	6.51	.	.	6.00	5.98
6.6	.	5.60	.	.	.	5.96	.	.	5.68	5.58
6.8	.	5.20	.	.	.	5.55	.	.	5.30	5.21
7.0	.	4.90	.	.	.	5.19	.	.	4.98	4.95
7.2	.	4.54	.	.	.	4.89	.	.	4.74	4.80
7.4	.	4.31	.	.	.	4.53	.	.	4.49	.
7.6	.	4.08	.	.	.	4.19	.	.	4.17	.
7.8	.	3.86	.	.	.	3.96	.	.	3.97	.
8.0	.	3.66	.	.	.	3.74	.	.	3.80	.
8.2	.	3.43	.	.	.	3.51	.	.	3.44	.
8.4	.	3.20	.	.	.	3.28
8.6	.	3.03	.	.	.	3.10
8.8	.	2.79	.	.	.	2.87
9.0	.	2.62	.	.	.	2.64
9.2	.	2.38	.	.	.	2.40
9.4	.	2.22	.	.	.	2.17
9.6	.	2.02	.	.	.	1.95
9.8	.	1.90	.	.	.	1.72
10.0	1.54
10.2	1.35
10.4	1.35

TABLE 6

$-\log_{10} V_a$ mol/l. min. Additions Present.

Series pH	1	2	3	4	5	6
	NaCl	NaCl	NaCl	NaCl	Na ₂ SO ₄	Na ₂ SO ₄
1.4
1.6
1.8
2.0
2.2
2.4
2.6
2.8
3.0	6.22
3.2	6.21	.	.	6.04	.	.
3.4	6.18	.	.	6.07	6.27	.
3.6	6.18	.	.	6.10	6.26	.
3.8	6.17	.	.	6.19	6.31	.
4.0	6.24	.	6.37	6.20	6.32	6.42
4.2	.	.	6.11	.	.	6.05
4.4	.	.	5.75	.	.	5.73
4.6	.	.	5.76	.	.	5.75
4.8	.	.	6.01	.	.	6.05
5.0	.	.	6.34	.	.	6.27
5.2	.	.	6.64	.	.	6.62
5.4	.	.	6.84	.	.	6.80
5.6	.	.	7.11	.	.	7.09
5.8
6.0
6.2	.	7.50
6.3	.	7.06
6.4	.	6.75
6.6	.	6.19
6.8	.	5.62
7.0	.	5.20
7.2	.	4.81
7.4	.	4.58
7.6	.	4.25
7.8	.	3.92
8.0	.	3.64
8.2	.	3.42
8.4	.	3.20
8.6	.	2.98
8.8	.	2.77
9.0	.	2.55
9.2	.	2.33
9.4	.	2.11
9.6	.	2.08
9.8	.	1.85
10.0	.	1.72
10.2	.	1.64
10.4	.	1.51
10.6	.	1.46
10.8

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$\beta = \frac{35.5 \times \alpha}{74.56}$ for the volume expansion as well as for the weight fraction of Cl in KCl. Each run of Table 4 is illustrated in Fig. 1 by a short horizontal line drawn over the range of pH-variation at the height of $\log_{10} V_a$.

Table 7 compares $\Delta[\text{Cl}^-]$ directly determined by titration of chloride ion and that calculated from associated pH before and after contact, from data given in Table 3; $\Delta[\text{Cl}^-]$ of run 1 in Table 3, conducted at high pH, was equated, according to (2.2) neglecting $[\text{H}^+]$, to the decrease of $[\text{OH}^-]$ determined by titration; $\Delta[\text{Cl}^-]$ of other runs in acidic region was that obtained in the successive approximation described in (i), § 2 from pH before and after contact; those runs of too small pH-shift were not quoted in Table 7. All concentrations there are referred to room temperature.

TABLE 7 $\Delta[\text{Cl}^-]$ by pH-Measurement and by Direct Titration

No. of run in Table 3	$\Delta[\text{Cl}^-]$ by pH-Measurement			$\Delta[\text{Cl}^-]$ Titrated	
	I N	I- $\Delta[\text{Cl}^-]$ N	$\Delta[\text{Cl}^-]$ N	Mohr's Method	Volhard's Method
1	3.27 *)	0.79 *)	2.48	2.30	2.15
7	-9.56×10^{-3}	-1.32×10^{-2}	0.0036	0.0044	0.0039
8	-9.56×10^{-3}	-2.32×10^{-2}	0.0136	0.0146	0.0134
9	-4.82×10^{-5}	-7.28×10^{-4}	0.0007	0.0010	0.0009
10	-4.82×10^{-5}	-3.04×10^{-3}	0.0030	0.0034	0.0028

*) I or I- $\Delta[\text{Cl}^-]$ in this case practically equals $[\text{OH}^-]$ titrated before or after contact respectively according to (2.2), $[\text{H}^+]$ being negligible in the strong alkaline solution.

Table 7 shows that the decomposition rate may be followed practically by pH-variation neglecting formate evolution as in §2, although runs except 1 in the Table conducted in acidic region, have not much to do with the validity of the neglect*), the error due to formate being suppressed there at any rate.

Fig. 1 shows that values of $\log_{10} V_a$ by different methods agree with each other in general features, although not quite quantitatively. The $\log_{10} V_a$ in general features is almost constant independent of pH at lower values. As pH increases, it begins to rise from a break at 3.2 pH with

*) Cf. foot-note *) on page 149.

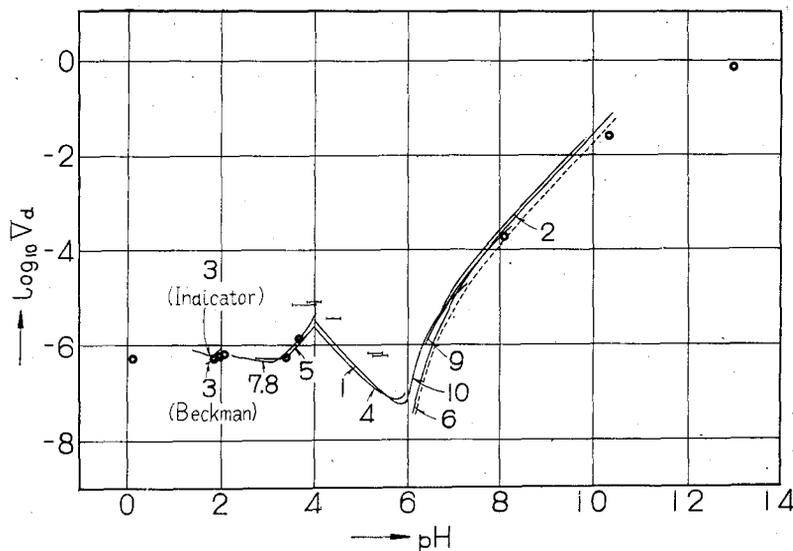


Fig. 1 Decomposition Rate of Chloroform Without Addition of Neutral Salt. (100°C).

- followed by pH, corrected for ionic interaction; associated number refers to series in Table 1.
- - - - followed by pH, not corrected.
- ⊙ " by titration.
- [] " by colorimetry.

an inclination near +1 up to a maximum, beyond which it descends to a minimum with an inclination near -1; from there on $\log_{10} V_d$ rises rather acutely toward larger pH with an inclination initially greater than +1 but falling with increasing pH gradually down to +1.

Fig. 2 shows on the other hand that the effect of the neutral salt is imperceptible at pH below the first break, whereas a definite depression between the break and maximum, an exaltation between the maximum and the minimum and again a depression above minimum.

§ 4. pH-Dependence without Neutral Salt Effect

It has been admitted in the foregoing paper⁵⁾ that chlorine exchange proceeded homogeneously in the interior of aqueous solution on the basis of the result that its rate is appreciably affected by pH-variation and that the addition of quartz powder made practically no difference

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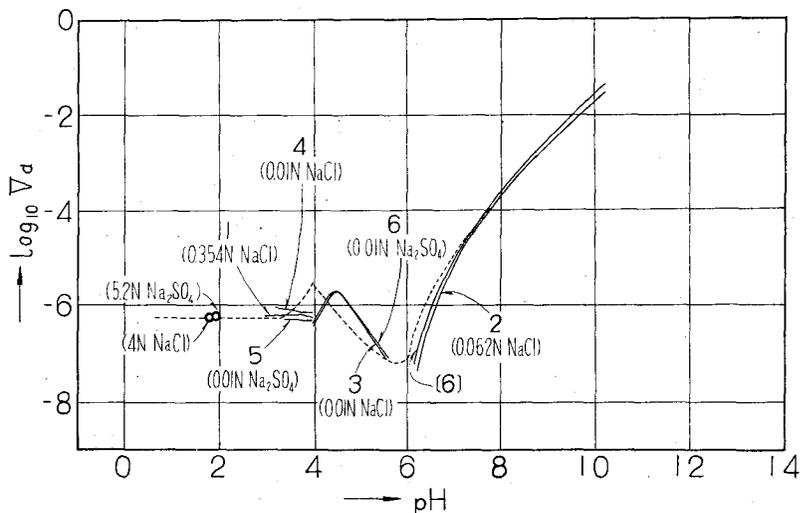


Fig. 2 Decomposition Rate of Chloroform with Addition of Neutral Salt (100°C).

- Rate in the presence of neutral salt; associated figure refers to series in Table 6, [6] to the 6th series of Table 5 and two circlets to the results of runs 11 and 12 of Table 3.
- - - - Average of $\log_{10} V_d$ without addition of neutral salt.
- Titration.

in its rate as shown by runs 16 and 17 in Table 3 in the foregoing paper⁵⁾ both conducted just under the same conditions except the addition of quartz powder in 17. It is seen from both the runs that pH decreases by just the same amount from 11.07 to 10.58 during the same contact time, which shows that the quartz powder does not affect the decomposition rate.

It will similarly be admitted that the decomposition proceeds homogeneously in the interior of aqueous solution along with the above result as well as with the observed appreciable pH effect on its rate.

The observed neutral salt effect on the decomposition rate cannot be due to that on the reverse rate of decomposition, inasmuch as the decomposition rate, for instance at pH 4.5, increases from 8.5×10^{-7} to 2×10^{-6} mol $\text{CHCl}_3/\text{min. lit. soln.}$ by 0.01 N NaCl or 0.01 N Na_2SO_4 addition as seen from the results of series 3 and 6 of Table 2 shown in Fig. 2, whereas the exchange rate, which gives the upper bound to the

reverse rate,^{*)} remains 2×10^{-9} mol. $\text{CHCl}_3/\text{min. lit. soln.}^{**)}$ at most, throughout.

The alternative is the effect through the forward rate. This cannot, however, be the mass effect of chloride ion or that due to the inclusion of chloride ion in any of the forward steps, since the decomposition rate varies but little from chloride concentration 0.01 N to 0.35 N as seen from series 1, 4 and 5 of Table 2 shown in Fig. 2 and moreover it is equally affected by 0.01 N Na_2SO_4 as mentioned above.^{***)}

The remaining possibility of the effect would be that of ionic interaction due to the neutral salt. On this basis the discrepancies between different series in Fig. 1 may be correlated with the observed neutral salt effect and henceforth the observed pH-dependence may be idealized at its absence or at its constant amount, if any, to get the pH-dependence ready for later analysis.

Consider the series of alkaline solution without addition of neutral salt. Hydrochloric acid liberated by decomposition does not practically vary the ionic strength of the solution but simply replaces hydroxide ion with chloride ion of the same amount, so long as pH lies sufficiently high above the neutral point.

The ionic strength begins to increase across the neutral point (6.11 according to the above K_a -value), resulting in depressing the $\log_{10} V_a$ versus pH curve downwards in accordance with the observed neutral salt effect there. Moreover the whole curve lies the lower, the higher the initial pH is. The discrepancies between curves in pH region above the neutral point in Fig. 1 are generally in conformity with this conclusion taking into account the inaccuracy associated with the measurement of short contact time especially at the beginning.

The $\log_{10} V_a$ curve at constant or zero ionic strength should hence have inclination in the neighbourhood of neutral point more or less

*) Reverse process of decomposition contributes definitely to the exchange [the flowing in of chlorine atom from solution to chloroform in one direction. Cf. §2 of the foregoing paper], but since the exchange may result otherwise as actually concluded in the foregoing paper, the observed exchange rate must be upper bound to the reverse rate.

***) Exchange rate observed in the foregoing paper was averaged at 5.8×10^{-7} $[\text{Cl}^-]$ mol $\text{Cl}/\text{min. lit.}$ One third of the latter rate or that referred to chloroform molecule must be compared with the decomposition rate given in the text. Since $[\text{Cl}^-]$ attains practically to 0.01 first at addition of 0.01 N NaCl , whereas it remains far smaller without it or at the addition of 0.01 N Na_2SO_4 , we arrived at data given in the text.

****) Cf. §5 of the foregoing paper.

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smaller than that observed. This conclusion is supported by the similar observation at 0°C, yet to be published,¹⁰⁾ in which $\log_{10} V_d$ could be determined accurately by the same method in different small pH-ranges separately at approximately the same ionic strength, because of smaller rate of decomposition. It has thus been found that $\log_{10} V_d$ at higher pH increased with almost +1 inclination.

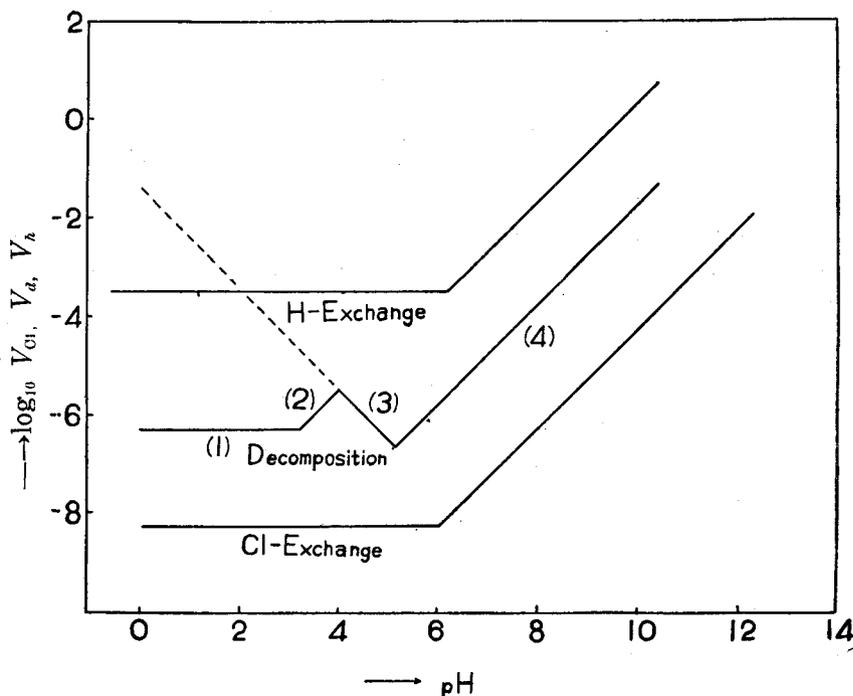


Fig. 3

On this ground it might be reasonable to idealize the experimental result as shown in Fig. 3 by a broken line "Decomposition" consisting of broken straight line (1), (2), (3) and (4) with inclination 0, 1, -1 and 1 respectively in the absence of varying neutral salt effect and to analyse the general features thus expressed in order to deduce the mechanism of reaction.

"H-Exchange" in Fig. 3 shows for comparison the rate V_h of hydrogen exchange recently observed by KANEKO and SATO and "Cl-Exchange" shows that V_{Cl} of chlorine exchange of the foregoing paper both occur-

ing under the same conditions as that of "Decomposition". Both "H-Exchange" and "Cl-Exchange" just cover the observed pH range respectively, although observed points are not plotted in the Figure.

The V_{O1} found proportional to $[Cl^-]$ in the foregoing paper was taken at 0.01 N $[Cl^-]$; "Cl-Exchange" in Fig. 3 hence gives the upper bound to the chlorine exchange rate under the condition of decomposition measurements without neutral salt addition made at $[Cl^-]$ around 0.01 N or less, from which the idealized figure was deduced.

§ 5. Postulates and Convention

Theory of steady reaction is developed below for analysis of the above experimental results on the basis of postulates (A) and (B) below,

(A) Over all reaction (termed simply reaction in what follows) is the resultant of a series Z of consecutive steps l 's^{*)} $l=1, \dots, n$; the initial complex^{**)} δ_i^i and the final complex^{***)} δ_i^f of every step l , except δ_i^i and δ_n^f , include each one intermediate^{***)} which is handed down from δ_{l-1}^f to δ_l^i , whereas δ_i^i and δ_n^f have no such intermediate.

Total number n of the steps is taken as at least 2.

It is understood that the chemical equation,

$$\delta^L = \delta^R$$

of the reaction is written so that the chemical potential μ^{δ^L} of the left δ^L is greater than that μ^{δ^R} of the right δ^R , i. e.,

$$\mu^{\delta^L} > \mu^{\delta^R} \quad (5.1)$$

such as,



for the chloroform decomposition and that its coefficients are so normalized that the reaction is identical with the resultant of Z .

Defining the absolute activity \mathcal{Q}^δ of any set δ of particles inclusive of δ^L and δ^R as,

$$RT \log \mathcal{Q}^\delta = \mu^\delta \quad (5.3)$$

*) The same notation is used for each step itself as well as for its number Z -series in what follows.

***) Initial or final complex of a step means the set of particles involved in the step at the state respectively before or after its occurrence.

****) Molecule or ion of short life formed intermediately in the course of reaction.

the present convention is stated as,

$$\mathcal{N}^{\delta^L} > \mathcal{N}^{\delta^R} \quad (5.4)$$

The forward or backward rate \bar{v}_i or \check{v}_i of a step l in homogeneous fluid is in general expressed as,*)

$$\bar{v}_i = k_i \mathcal{N}^{\delta_i^I}, \quad \check{v}_i = k_i \mathcal{N}^{\delta_i^F} \quad (5.5. I) \quad (5.5. F)$$

where the common factor k_i to \bar{v}_i and \check{v}_i depends on the composition of the assembly in which the reaction is going on and in general even on the amount and hence on the activity of intermediates. It is postulated in what follows that,

(B) k_i is independent of the activity of intermediates.

§ 6. Steady Reaction in General

Several fundamental conclusions will be deduced below from postulates in the foregoing section.

$$(I) \quad \frac{\prod_{l=1}^{l=n} \mathcal{N}^{\delta_l^I}}{\prod_{l=1}^{l=n} \mathcal{N}^{\delta_l^F}} = \frac{\mathcal{N}^{\delta^L}}{\mathcal{N}^{\delta^R}} \quad (6.1)$$

A complete set of δ_l^I 's and that of δ_l^F 's should include the same number each of those molecules and ions according to (A), inclusive of intermediates, which are involved in the

*) The forward and backward rates \bar{v} and \check{v} reckoned to unit volume are given as,

$$\bar{v} = \kappa \frac{kT}{h} \cdot \frac{Q^{\delta^*}}{p^{\delta^I}}, \quad \check{v} = \kappa \frac{kT}{h} \cdot \frac{Q^{\delta^*}}{p^{\delta^F}}$$

for a step in a homogeneous fluid [Cf. HORIUTI; Jour. Res. Inst. Catalysis, Hokkaido Univ. 1, 8 (1948), §24, Eq. (24.8 \bar{v}) and (24.8 \check{v}); suffix 1 to \bar{v} and \check{v} in the original is omitted here], where Q^{δ^*} is the partition function of the critical complex δ^* [Cf. Eq. (24.5) *ibid.*]; the p^{δ} is the BOLTZMANN factor of μ^{δ} [Cf. §7, *ibid.*], or the reciprocal absolute activity according to (5.3), so that we have (5.5) with common factor k to \bar{v} and \check{v} , i. e.,

$$k_l = \kappa \frac{kT}{h} Q^{\delta^*} \quad \text{or} \quad k_l = k_{l,0} / f^{\delta^*}$$

where,

$$k_{l,0} = \kappa \frac{kT}{h} Q_0^{\delta^*} \quad \text{and} \quad f^{\delta^*} = Q_0^{\delta^*} / Q^{\delta^*}$$

is the statistical mechanical expression for the activity coefficient of the critical complex δ^* of the step and $Q_0^{\delta^*}$ the particular value of Q^{δ^*} at infinite dilution of components of variable concentration [Cf. §28 *ibid.*].

reaction but neither consumed nor generated after all, because each of them should appear in δ_i^I 's and in δ_i^F 's just the same number of times. The fraction on the left of (6.1) is hence reduced to that on the right.

(II) Steady reaction rate V_s is given according to (A) and (5.5) as,

$$V_s = k_l (\mathfrak{A}_s^{\delta_l^I} - \mathfrak{A}_s^{\delta_l^F}) \quad l = 1, 2, \dots, n \quad (6.2. V)$$

where suffix s denotes the particular value at the steady state, whereas,

$$\mathfrak{A}_s^{\delta_l^I} = \mathfrak{A}^{\delta_l^I}, \quad \mathfrak{A}_s^{\delta_l^F} = \mathfrak{A}^{\delta_l^F} \quad (6.2. I) \quad (6.2. F)$$

are respectively definite, irrespective of the activity of intermediates according to (A) in a definite composition of the homogeneous fluid with regard to stable molecules and ions.

$$(III) \quad V_s > 0 \quad (6.3)$$

inasmuch as the assumption,

$$V_s \leq 0$$

leads according to (6.2. V) and (6.1) to the conclusion,

$$\mathfrak{A}^{\delta^L} / \mathfrak{A}^{\delta^R} \leq 1$$

in contradiction to (5.4), because,

$$k_l > 0, \quad l = 1, 2, \dots, n$$

by definition.

$$(IV) \quad \frac{\mathfrak{A}_{e,j}^{\delta_j^I}}{\mathfrak{A}_{e,j}^{\delta_j^F}} = \frac{\mathfrak{A}^{\delta^L}}{\mathfrak{A}^{\delta^R}} \quad (6.4)$$

where $\mathfrak{A}_{e,j}^{\delta_j^I}$ or $\mathfrak{A}_{e,j}^{\delta_j^F}$ is respectively the particular value of $\mathfrak{A}^{\delta_j^I}$ or $\mathfrak{A}^{\delta_j^F}$ subject to the condition,

$$\mathfrak{A}_{e,j}^{\delta_l^I} = \mathfrak{A}_{e,j}^{\delta_l^F}, \quad l = 1, \dots, j-1, j+1, \dots, n \quad (6.5. \mathfrak{A})$$

$\mathfrak{A}_{e,j}^{\delta_j^I}$ or $\mathfrak{A}_{e,j}^{\delta_j^F}$ being respectively of fixed value according to (A), i. e.,

$$\mathfrak{A}_{e,j}^{\delta_l^I} = \mathfrak{A}^{\delta_l^I}, \quad \mathfrak{A}_{e,j}^{\delta_l^F} = \mathfrak{A}^{\delta_l^F} \quad (6.5. I) \quad (6.5. F)$$

Condition (6.5. \mathfrak{A}) states that all steps but j -th one are in equilibrium in accordance with definition (5.3) of absolute activity.

Eq. (6.4) is derived readily from (6.1) and (6.5. \mathfrak{A}).

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$$(V) \quad \mathfrak{A}_{e,j(>l)}^{\delta I} = \mathfrak{A}_{e,j(>l)}^{\delta F} = \mathfrak{A}_{e,l}^{\delta I}, \quad \mathfrak{A}_{e,j'(<l)}^{\delta I} = \mathfrak{A}_{e,j'(<l)}^{\delta F} = \mathfrak{A}_{e,l}^{\delta F} \quad (6.6. I) \quad (6.6. F')$$

This relation follows from (A), (B) and (6.5) since the activity of the intermediate included in δI^I or $\delta I^{F'}$ is the only variable factor in $\mathfrak{A}^{\delta I}$ or in $\mathfrak{A}^{\delta F'}$ respectively at constant activities of stable molecules and ions according to (A), and hence uniquely determined by first l equations or last $n-l+1$ ones of (6.5. A) according as $l < j$ or $l > j$ respectively, according to (B) irrespective of the activities of the rest of the intermediates.

$$(VI) \quad \frac{\mathfrak{A}_{e,j(\geq l)}^{\delta I}}{\mathfrak{A}_{e,j'(<l)}^{\delta I}} = \frac{\mathfrak{A}_{e,j(\geq l)}^{\delta F-1}}{\mathfrak{A}_{e,j'(<l)}^{\delta F-1}} = \frac{\mathfrak{A}^{\delta L}}{\mathfrak{A}^{\delta R}} \quad (6.7)$$

This relation which follows immediately from (IV) and (V) means that $\mathfrak{A}_{e,j}^{\delta I}$ remaining invariant in the region $j \geq l$ or $j < l$ of j respectively, increases by a factor $\mathfrak{A}^{\delta L}/\mathfrak{A}^{\delta R}$ as j passes from the latter to the former region and that the same is true with $\mathfrak{A}_{e,j}^{\delta F-1}$.

$$(VII) \quad \frac{1}{V_S} = \sum_{i=1}^{i=n} \frac{1}{V_{e,i}} \quad (6.8. S)$$

where,

$$V_{e,i} = k_i (\mathfrak{A}_{e,i}^{\delta I} - \mathfrak{A}_{e,i}^{\delta F}) \quad (6.8. l)$$

We have,

$$\kappa_i = \frac{\mathfrak{A}_S^{\delta F-1}}{\mathfrak{A}_S^{\delta I}} = \frac{\mathfrak{A}_{e,i}^{\delta F-1}}{\mathfrak{A}_{e,i}^{\delta I}}$$

inasmuch as the only variable factor of $\mathfrak{A}_{e,i}^{\delta I}$ or of $\mathfrak{A}_S^{\delta I}$, which makes difference between them, is the activity of the intermediate commonly implied in $\mathfrak{A}_{e,i}^{\delta F-1}$ according to (A), and hence, equating $\mathfrak{A}_{e,i}^{\delta F-1}$ to $\mathfrak{A}_{e,i}^{\delta I}$ according to (6.6. I),

$$\kappa_i = \frac{\mathfrak{A}_S^{\delta F-1}}{\mathfrak{A}_S^{\delta I}} = \frac{\mathfrak{A}_{e,i}^{\delta I-1}}{\mathfrak{A}_{e,i}^{\delta I}} \quad (6.9. I)$$

We have on the other hand by similar reasoning,

$$\kappa_i = \frac{\mathfrak{A}_S^{\delta F-1}}{\mathfrak{A}_S^{\delta I}} = \frac{\mathfrak{A}_{e,i}^{\delta F-1}}{\mathfrak{A}_{e,i}^{\delta I-1}}$$

and henceforth equating $\mathfrak{A}_{e,i}^{\delta I}$ to $\mathfrak{A}_{e,i}^{\delta F}$ according to (6.6. F'),

$$\kappa_i = \frac{\mathfrak{A}_S^{\delta F-1}}{\mathfrak{A}_S^{\delta I}} = \frac{\mathfrak{A}_{e,i}^{\delta I-1}}{\mathfrak{A}_{e,i}^{\delta F}} \quad (6.9. F')$$

Defining $K_l, l=0, \dots, n$ as,

$$K_0 = K_1 = 1, \quad K_2 = \kappa_2, \dots, K_l = \prod_{i=2}^{l-1} \kappa_i \quad (6.10. K)$$

we have from (6.9) and (6.5),

$$K_l \mathfrak{A}_{e,l}^{\delta_l^I} = \mathfrak{A}^{\delta_l^I}, \quad \frac{K_n}{K_l} \mathfrak{A}^{\delta_n^F} = \mathfrak{A}_{e,l}^{\delta_l^F} \quad (6.10. I) \quad (6.10. F)$$

and henceforth according to (6.2.V), (6.8.l) and (6.9),

$$\frac{V_S}{V_{e,l}} = \frac{\mathfrak{A}_S^{\delta_l^I} - \mathfrak{A}_S^{\delta_l^F}}{\mathfrak{A}_{e,l}^{\delta_l^I} - \mathfrak{A}_{e,l}^{\delta_l^F}} = \frac{K_l (\mathfrak{A}_S^{\delta_l^I} - \mathfrak{A}_S^{\delta_l^F})}{K_l (\mathfrak{A}_{e,l}^{\delta_l^I} - \mathfrak{A}_{e,l}^{\delta_l^F})} = \frac{K_{l-1} \mathfrak{A}_S^{\delta_{l-1}^F} - K_l \mathfrak{A}_S^{\delta_l^F}}{\mathfrak{A}_S^{\delta_l^I} - K_n \mathfrak{A}_n^{\delta_n^F}}$$

Summing up and remembering (6.2) we have,

$$\begin{aligned} \sum_{l=1}^{l=n} \frac{V_S}{V_{e,l}} &= \frac{\mathfrak{A}_S^{\delta_1^I} - \mathfrak{A}_S^{\delta_1^F}}{\mathfrak{A}_S^{\delta_1^I} - K_n \mathfrak{A}_n^{\delta_n^F}} + \frac{\mathfrak{A}_S^{\delta_1^F} - K_2 \mathfrak{A}_S^{\delta_2^F}}{\mathfrak{A}_S^{\delta_1^I} - K_n \mathfrak{A}_n^{\delta_n^F}} + \dots + \frac{K_{l-2} \mathfrak{A}_S^{\delta_{l-2}^F} - K_{l-1} \mathfrak{A}_S^{\delta_{l-1}^F}}{\mathfrak{A}_S^{\delta_1^I} - K_n \mathfrak{A}_n^{\delta_n^F}} \\ &+ \frac{K_{l-1} \mathfrak{A}_S^{\delta_{l-1}^F} - K_l \mathfrak{A}_S^{\delta_l^F}}{\mathfrak{A}_S^{\delta_1^I} - K_n \mathfrak{A}_n^{\delta_n^F}} + \dots + \frac{K_{n-2} \mathfrak{A}_S^{\delta_{n-2}^F} - K_{n-1} \mathfrak{A}_S^{\delta_{n-1}^F}}{\mathfrak{A}_S^{\delta_1^I} - K_n \mathfrak{A}_n^{\delta_n^F}} + \frac{K_{n-1} \mathfrak{A}_S^{\delta_{n-1}^F} - K_n \mathfrak{A}_S^{\delta_n^F}}{\mathfrak{A}_S^{\delta_1^I} - K_n \mathfrak{A}_n^{\delta_n^F}} \\ &= 1 \end{aligned} \quad (6.11)$$

which proves (6.8).

$$(VIII) \quad V_{e,l} > V_S \quad (6.12)$$

This relation follows immediately from the foregoing one, which states,

$$\frac{1}{V_S} > \frac{1}{V_{e,l}}$$

inasmuch as all $V_{e,l}$'s are positive according to (5.4), (6.4) and (6.8.l).

(IX) As one of $V_{e,l}$ ($l=j$) decreases leaving all other $V_{e,l}$'s ($l \neq j$) constant, $\mathfrak{A}_S^{\delta_l^I}$ or $\mathfrak{A}_S^{\delta_l^F}$ ($l=1, \dots, n$) approaches $\mathfrak{A}_{e,j}^{\delta_j^I}$ or $\mathfrak{A}_{e,j}^{\delta_j^F}$ respectively.

The l -th term ($l=1, \dots, n$) in the second member of (6.11) denoted by (l) gives $V_S/V_{e,l}$ as stated there. As one of $V_{e,l}$'s ($l=j$) decreases, the term tends to 1, while others to 0, inasmuch as all terms are positive according to (6.3) and (6.12) and their sum is 1 according to (6.8.s).

The sum of the first $l-1$ ($l < j$) terms,

$$\frac{\mathfrak{A}_S^{\delta_l^I} - K_{l-1} \mathfrak{A}_S^{\delta_{l-1}^F}}{\mathfrak{A}_S^{\delta_l^I} - K_n \mathfrak{A}_n^{\delta_n^F}}$$

or its numerator $\mathfrak{A}_S^{\delta_l^I} - K_{l-1} \mathfrak{A}_S^{\delta_{l-1}^F}$ should hence tend to zero, so that $\mathfrak{A}_S^{\delta_{l-1}^F}$ tends to $\mathfrak{A}_S^{\delta_l^I}/K_{l-1}$, which equals $\mathfrak{A}_{e,l}^{\delta_l^F}$ according to (6.10. I) and (6.6. I).

The Mechanism of the Decomposition of Chloroform

Rewriting the same numerator by (6.9. I) and (6.10. K) as,

$$\mathfrak{N}^{\delta_i^I} - K_i \mathfrak{N}_S^{\delta_i^I}$$

we see similarly by (6.10. I) and (6.6. I) that $\mathfrak{N}_S^{\delta_i^I}$ tends to $\mathfrak{N}_{e,j(>l)}^{\delta_i^I}$, as $V_{e,j}$ does to zero.

It may be shown similarly that $\mathfrak{N}_S^{\delta_i^I}$ or $\mathfrak{N}_S^{\delta_i^{I'}}$ approaches respectively $\mathfrak{N}_{e,j}^{\delta_i^I}$ or $\mathfrak{N}_{e,j}^{\delta_i^{I'}}$ for $j < l$, so that the above proposition (IX) holds.

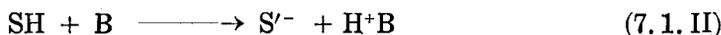
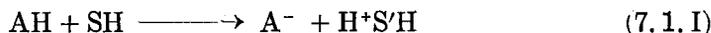
(X) *If two intermediates in Z-series are identical with each other, all $1/V_{e,i}$ terms in (6.8. S) of steps, which intervene between the two, vanish.*

Let $l', l'+1, \dots, l''$ be steps which intervene between any two identical intermediates. The κ_i is now, according to (6.9. I), the activity of the set of particles to be added to $\delta_{l'}^I$ to form $\delta_{l'-1}^{I'}$. The product $\prod_{i=l'}^{l''} \kappa_i = \frac{K_{l''}}{K_{l'-1}}$ in accordance with (6.10. K) is hence the activity of the whole set of particles required to be added to $\delta_{l''}^I$, or $\delta_{l''}^{I'}$, for forming $\delta_{l'-1}^{I'}$, as $\delta_{l'}^I$ and $\delta_{l''}^{I'}$ consist in general of the same set of particles. $K_{l'-1} \mathfrak{N}_S^{\delta_{l'-1}^{I'}}$ in (l')-term in the summation of (6.11) is now identical with $K_{l''} \mathfrak{N}_S^{\delta_{l''}^{I'}}$, inasmuch as the intermediate in $\delta_{l'-1}^{I'}$ handed down to $\delta_{l'}^I$ according to (A), is identical with that included in $\delta_{l''}^{I'}$ by the present premise. It follows that the sum $\sum_{i=l'}^{l''} \frac{V_S}{V_{e,i}}$ vanishes as seen from the second member of (6.11). But since $V_{e,i}$'s and V_S are respectively positive according to (6.3) and (6.12), every term included and hence the corresponding term in (6.8. S) should vanish individually as stated in the above proposition (X).

§ 7. Rate of Proton Transfer

We now postulate that,

(C) *Any step involving proton transfer is of the three types,*



where AH or B is BRÖNSTED's acid or base respectively, SH the substrate, which turns into $\text{H}^+\text{S}'\text{H}$, S'^- or HS' respectively and S' a set of particles into which S of SH in general converted; AH is of two kinds, H_2O and H_3O^+ , and B similarly OH^- and H_2O respectively exclusively, two acids or two bases concurrently taking part in (7.1) in bringing about the identical change in SH.

Step (7.1.I) etc. will be denoted by I etc. respectively and one of these steps represented by I' .

The sum of concurrent forward rates $\bar{v}(I')$ or that of concurrent

backward rates $\bar{v}(\Gamma)$ of Γ is expressed as,

$$\bar{v}(\text{I}) = k(\text{I}) \mathfrak{A}^{\text{SH}}, \quad \bar{v}(\text{I}) = k(\text{I}) \mathfrak{A}^{\text{H}^+\text{S}^-\text{H}} \mathfrak{A}^{\text{OH}^-} / \mathfrak{A}^{\text{H}_2\text{O}} \quad (7.2. \bar{v}) (7.2. \bar{v})$$

$$k(\text{I}) = \left\{ k(\text{I}, \text{H}_2\text{O}) + k(\text{I}, \text{H}_3\text{O}^+) \frac{\mathfrak{A}^{\text{H}^+}}{\mathfrak{A}^{\text{H}_2\text{O}}} \right\} \mathfrak{A}^{\text{H}_2\text{O}} \quad (7.2. k)$$

$$\bar{v}(\text{II}) = k(\text{II}) \mathfrak{A}^{\text{SH}}, \quad \bar{v}(\text{II}) = k(\text{II}) \mathfrak{A}^{\text{S}^-\text{H}^+\text{H}} / \mathfrak{A}^{\text{H}_2\text{O}} \quad (7.3. \bar{v}) (7.3. \bar{v})$$

$$k(\text{II}) = \left\{ k(\text{II}, \text{OH}^-) \frac{\mathfrak{A}^{\text{H}_2\text{O}}}{\mathfrak{A}^{\text{H}^+}} + k(\text{II}, \text{H}_2\text{O}) \right\} \mathfrak{A}^{\text{H}_2\text{O}} \quad (7.3. k)$$

$$\bar{v}(\text{III}) = k(\text{III}) \mathfrak{A}^{\text{SH}}, \quad \bar{v}(\text{III}) = k(\text{III}) \mathfrak{A}^{\text{HS}^-\text{H}} \quad (7.4. \bar{v}) (7.4. \bar{v})$$

$$k(\text{III}) = \left\{ k(\text{III}, \text{H}_2\text{O}, \text{H}_2\text{O}) + k(\text{III}, \text{H}_3\text{O}^+, \text{OH}^-) + k(\text{III}, \text{H}_3\text{O}^+, \text{H}_2\text{O}) \frac{\mathfrak{A}^{\text{H}^+}}{\mathfrak{A}^{\text{H}_2\text{O}}} \right. \\ \left. + k(\text{III}, \text{H}_2\text{O}, \text{OH}^-) \frac{\mathfrak{A}^{\text{H}_2\text{O}}}{\mathfrak{A}^{\text{H}^+}} \right\} (\mathfrak{A}^{\text{H}_2\text{O}})^2 \quad (7.4. k)$$

where $\mathfrak{A}^{\text{H}^+}$ is the absolute activity of H_3O^+ and $k(\text{I}, \text{AH})$ or $k(\text{II}, \text{B})$ or $k(\text{III}, \text{AH}, \text{B})$ represents respectively the particular value of k_i of step Γ caused by particular AH or B or by particular combination of AH and B indicated in parenthesis.

The above expressions are derived as follows. The forward rate $\bar{v}(\text{I}, \text{H}_2\text{O})$ or $\bar{v}(\text{I}, \text{H}_3\text{O}^+)$ of I involving acid H_2O or H_3O^+ respectively is expressed according to (5.5. I) as,

$$\bar{v}(\text{I}, \text{H}_2\text{O}) = k(\text{I}, \text{H}_2\text{O}) \mathfrak{A}^{\text{H}_2\text{O}} \mathfrak{A}^{\text{SH}}$$

$$\bar{v}(\text{I}, \text{H}_3\text{O}^+) = k(\text{I}, \text{H}_3\text{O}^+) \mathfrak{A}^{\text{H}^+} \mathfrak{A}^{\text{SH}}$$

which gives the total forward rate, $\bar{v}(\text{I}) = \bar{v}(\text{I}, \text{H}_2\text{O}) + \bar{v}(\text{I}, \text{H}_3\text{O}^+)$ of (7.2. \bar{v}). The corresponding backward rate $\bar{v}(\text{I}, \text{H}_2\text{O})$ or $\bar{v}(\text{I}, \text{H}_3\text{O}^+)$ is similarly given by (5.5. F) and (7.1. I) as,

$$\bar{v}(\text{I}, \text{H}_2\text{O}) = k(\text{I}, \text{H}_2\text{O}) \mathfrak{A}^{\text{H}^+\text{S}^-\text{H}} \mathfrak{A}^{\text{OH}^-}$$

$$\bar{v}(\text{I}, \text{H}_3\text{O}^+) = k(\text{I}, \text{H}_3\text{O}^+) \mathfrak{A}^{\text{H}^+\text{S}^-\text{H}} \mathfrak{A}^{\text{H}_2\text{O}}$$

the conjugate base of acid H_2O or H_3O^+ being respectively OH^- or H_2O . The total backward rate is now obtained from the above two equations as given by (7.2. \bar{v}) taking the equilibrium relation,

$$\mathfrak{A}^{\text{H}^+} \mathfrak{A}^{\text{OH}^-} = (\mathfrak{A}^{\text{H}_2\text{O}})^2 \quad (7.5)$$

of the dissociation of water into account.

Eqs. (7.3) and (7.4) may similarly be derived.

(XI) We see that, $\bar{v}(\Gamma)$ or $\bar{v}(\Gamma)$ is expressed with the common factor $k(\Gamma)$ just as in the case of (5.5) although different acids, bases or their combinations concurrently take part in the step and that $k(\Gamma)$ is independent of any intermediate's activity by (7.2.k) etc., inasmuch as it is the case with the individual k_i 's involved according to (B). All conclusions arrived at in §6 remain valid for Z including Γ among its constituent steps, the part of δ_i^Z or k_i in §6 being formally assigned to SH or $k(\Gamma)$ respectively.

§ 8. Rules for Analysis

Several rules are now deduced for the sake of later analysis of experimental results from the foregoing general theoretical conclusions and following assumptions a) and b) particular to chloroform decomposition.

a) Chloroform decomposes through Z-series of (A), including Γ .

b) Only one chloroform molecule is included in the initial complex of the first step of Z but none in initial or final complexes of all other steps.

It follows from a), (6.4) and (5.3),

$$i) \quad \mathcal{N}_{e,l}^{\delta^I} \gg \mathcal{N}_{e,l}^{\delta^F}, \quad l = 1, 2, \dots, n \quad (8.1)$$

admitting that,

$$\mu^{\delta^Z} \gg \mu^{\delta^R}$$

for the chloroform decomposition (5.2) under the present experimental conditions.

The $V_{e,l}$ may hence be written according to (6.8.1) neglecting $\mathcal{N}_{e,l}^{\delta^F}$ as,

$$V_{e,l} = k_l \mathcal{N}_{e,l}^{\delta^I} \quad (8.2)$$

or particularly for steps of proton transfer according to (7.2), (7.3) and (7.4) as,

$$V_{e,l}(\Gamma) = k_l(\Gamma) a_{e,l}^{\text{SH}^I}, \quad \Gamma = \text{I, II, III} \quad (8.3)$$

where,

$$k(\text{I})_l = k_{A,l}^{\text{W}} + k_{A,l}^{\text{H}^+} a^{\text{H}^+} \quad (8.4. \text{I})$$

$$k(\text{II})_l = k_{B,l}^{\text{W}} + k_{B,l}^{\text{OH}^-} / a^{\text{H}^+} \quad (8.4. \text{II})$$

$$k(\text{III})_l = k_{A,B,l} + k_l^{\text{H}^+} a^{\text{H}^+} + k_l^{\text{OH}^-} / a^{\text{H}^+} \quad (8.4. \text{III})$$

and $k_{A,l}^{\text{W}}$ etc. are quantities respectively proportional to $k(\text{I}, \text{H}_2\text{O})$ etc. of Γ -type steps now included in Z as l -th ones; they have, besides $\mathcal{N}^{\text{H}_2\text{O}}$ or $(\mathcal{N}^{\text{H}_2\text{O}})^2$, an unimportant conversion factor for reducing absolute activity \mathcal{N}^{SH} or \mathcal{N}^{H^+} to usual one a^{SH} or a^{H^+} respectively normalized to concentration at infinite dilution as their factor, and are respectively constant independent of a^{H^+} or of ionic strength, in so far as $k(\text{I}, \text{H}^+)$ etc. in (7.2), (7.3) and (7.4) as well as $a^{\text{H}_2\text{O}}$ are constant. They are assumed respectively constant in analysing the idealized pH dependence of Fig. 3 obtained from direct experimental results by eliminating the

effect of ionic interaction as far as possible to deduce the mechanism; $k_{A,l}^{\nu}$ etc. will later be allowed for the variation due to the ionic interaction according to the relation,

$$k_l = k_{l,0}/f^{\delta^*} \quad (8.5)$$

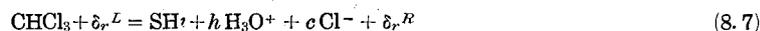
in accounting for the deviation of the direct experimental results from the idealized one on the basis of the mechanism.

ii) $\mathcal{N}_{e,l}^{\text{SH}_l}$ is proportional to $\mathcal{N}^{\text{CHCl}_3} (\mathcal{N}^{\text{H}^+})^{-h_l} (\mathcal{N}^{\text{Cl}^-})^{-c_l}$, i. e.,

$$\mathcal{N}_{e,l}^{\text{SH}_l} \propto \mathcal{N}^{\text{CHCl}_3} (\mathcal{N}^{\text{H}^+})^{-h_l} (\mathcal{N}^{\text{Cl}^-})^{-c_l} \quad (8.6)$$

where h_l or c_l is the total number of protons or chloride ions discharged by chloroform molecule in the initial complex of the first step, as it converts into SH_l .

Eq. (8.6) is deduced as below. The first $l-1$ steps of Z , which provide SH_l from the single chloroform molecule, ought to be respectively in equilibrium with regard to condition (6.5.9) associated with the definition of $\mathcal{N}_{e,l}^{\text{SH}_l}$. Let their resultant be expressed in the form of the chemical equation,



where $\delta_{r,L}$ or $\delta_{r,R}$ is the remainder of molecules or ions on the left or right of the "chemical equation", which includes none of CHCl_3 , H_3O^+ and Cl^- according to a), b) and the above premise. The reaction of the latter chemical equation being in equilibrium because of the equilibrium of constituent steps, we have the absolute activities of its left and right equal to each other or (8.6).

It follows now from (8.6) and (b) that,

iii) $V_{e,l}$ is proportional to $\mathcal{N}^{\text{CHCl}_3}$ and hence V_S too according to (8.2) and (6.8.S), i. e., the decomposition proceeds in first order with respect to chloroform.

HINE¹¹⁾ and SAUNDERS¹²⁾ have shown that the decomposition was first order with respect to chloroform in 66% aqueous dioxane and in 95% alcohol, which seems to support the above conclusion and hence the underlying assumptions a) and b).

It follows on the other hand from (8.6) that,

(iv) $\mathcal{N}_{e,l}^{\text{SH}_l}$ is inversely proportional to $(\mathcal{N}^{\text{H}^+})^{h_l}$, which completes according to (8.4) the pH-dependence of $V_{e,l}(\Gamma)$.

Fig. 4 shows the pH-dependence of $V_{e,l}(\Gamma)$ thus obtained, by broken line, from which it deviates upwards by $\log 2$ at most in the neighbourhood of each break, where two terms on the right of (8.4) nearly equal each other. Fig. 4, (III_a) or (III_b) shows the pH-dependence of $V_{e,l}(\Gamma)$ in the case when k_{ABl} on the right of (8.4.III) is sufficiently large, so that $k(\text{III})_l$ remains practically constant for a certain pH-range, or not, respectively.

*) Cf. foot-note on page 167.

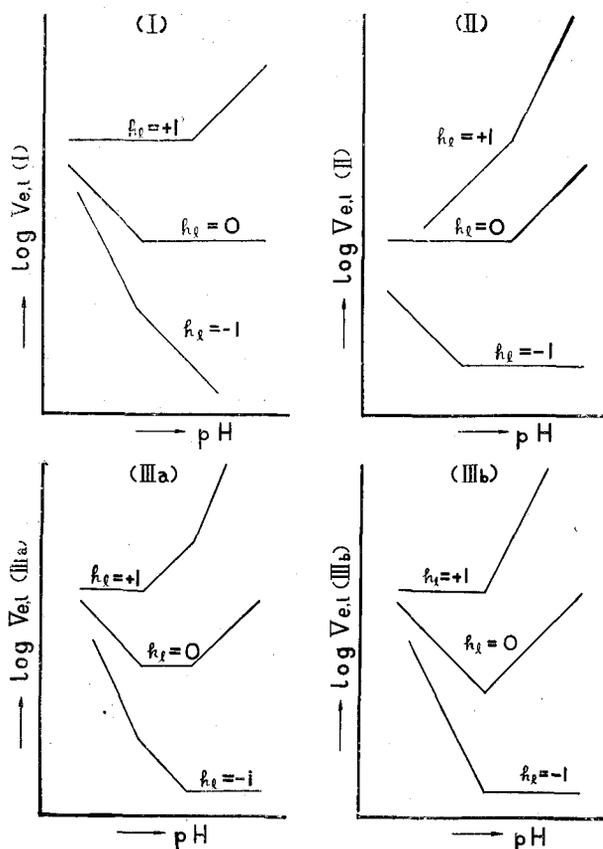


Fig. 4 pH-Dependence of $\log_{10} V_{e,i}(\Gamma)$
 $\Gamma = \text{I, II, III}_a, \text{III}_b,$

We will denote the step of different Γ and h_i by $\Gamma(h_i)$ as I(+1) or III_b(0) and the appropriate $V_{e,i}$ by $V_{e,i}(\Gamma, h_i)$ as $V_{e,i}(\text{I}, +1)$ or $V_{e,i}(\text{III}_b, 0)$.

It follows now from (6.12), (6.8.S) and (XI), §7 that,

v) if one of the $V_{e,i}$'s is sufficiently small compared with all others, it practically equals V_s , or, in other words, l becomes the rate-determining step and that if some of them, g in number, nearly equal to each other, are sufficiently smaller than the others V_s equals practically one g -th each of them.

Lowest $V_{e,i}$ may be taken approximately V_s under any condition, if we are contented with the order of magnitude in the neighbourhood of the points, where a few $V_{e,i}$'s approach each other; along with this approximation, we might call in what follows more or less conventio-

nally, step l of lowest $V_{e,l}$, the rate-determining step.

It follows from this approximation, that,

(vi) *pH-dependence of V_s may be graphically synthesized from those of $V_{e,l}$ by drawing $\log V_{e,l}$ vers. pH diagrams together on one sheet and reserving lowest line only as giving V_s or $V_{e,j}$ of the rate-determining step j at every pH.*

Further conclusions are drawn with regard to Fig. 4 and to the above method of synthesis as below :

vii) *upward convexity inclusive of maximum of V_s corresponds to the change of the role of determining the rate from one step to another;*

viii) *straight or upward concave part inclusive of minimum corresponds to the same rate-determining step prevailing thereabout, and as seen from Fig. 4,*

ix) *the minimum, in particular, corresponds uniquely to III_b(0) determining the rate;*

x) *if step l leads the rate-determining step j in Z-series or $l < j$, it has forward and backward rates balanced with each other and equal to $V_{e,l}$ according to (IX), (6.5.9), (5.5) and (8.2), whereas if $l > j$, then the balanced forward and backward rates reduce to $\eta^{\delta^R}/\eta^{\delta^L}$ times $V_{e,l}$ according to (VI), i. e., to an extremely small value compared with $V_{e,l}$ according to (8.1).*

xi) *Such step as intervening between identical intermediates is never significant in the above synthesis, inasmuch as the appropriate term $1/V_{e,l}$ in (6.8.S), through which the step substantially enters the latter synthesis, is missing according to (X).*

§ 9. Analysis of Experimental Results

We will proceed to analyse the experimental result illustrated in Fig. 3 by means of rules prepared in the foregoing section identifying V_a with V_s now in accordance with (a).

It is first concluded that the rate-determining step around the minimum is a step of type III_b(0) according to (ix), which switches over into some other one across the maximum according to (vii) and that the latter persists over pH values below that of the maximum according to (viii) and Fig. 3. The rate-determining step at higher or lower pH values as well as its number in Z-series will be denoted respectively by III or Y.

We will first discuss the case when III leads Y in Z-series. Let C be the step, in which the first chlorine atom of chloroform is dis-

charged into the solution in the form of a chloride ion. If C leads Y in Z -series, steps $l \leq C$ are all in equilibrium and occurring back and forth respectively at rates $V_{e,1}, \dots, V_{e,l}, \dots, V_{e,c}$ according to (x), over the pH-range where Y determines the rate. Since chlorine atom picked up by the reversal of C is brought back into chloroform at a rate of the lowest value of $V_{e,1}, \dots, V_{e,c}$ *) and the latter are all greater than $V_{e,Y}$ according to (vi), it follows that chloride ion exchange proceeds more quickly than the decomposition determined at $V_{e,Y}$. This conclusion contradicts the experimental result shown in Fig. 3 that the decomposition rate exceeds considerably the chlorine exchange rate. Admitting that chlorine is discharged from chloroform, if at all, only in the form of chloride ion, it follows that CCl_3 -skeleton of chloroform is handed down unchanged to the initial complex of Y .

Step III implies on the other hand the exchange of hydrogen, whose contribution to the total hydrogen exchange rate is similarly equal to or less than the lowest of the $V_{e,i}$'s of all steps from 1 to III.**)

If III happens to be the first step of Z , $V_{e,\text{III}}$ itself would be the lower bound to the observed hydrogen exchange rate, inasmuch as it may be effected through other channel as well. This lower bound is illustrated by dotted line, i. e., by the elongation of the branch of III at lower pH in Fig. 3. The observed hydrogen exchange rate as seen in the Figure lies definitely below it. It follows that III has at least one step preceding in Z -series.

It has been concluded above that the CCl_3 -skeleton of chloroform must be kept unchanged throughout steps down to the initial complex of Y , but the basis for this conclusion does not exclude the possibility of the skeleton picking up some chloride ion to form the initial complex of III, without affording the latter a position equivalent

*) Let x_c be the fraction of chlorine atoms in the initial complex of C , which have come from solution directly without once getting into chloroform, x_{c-1} that of the step preceding C and so on; x_1 must then be assigned to zero.

We have now,

$$\begin{aligned} V_{e,c}(1-x_c) &= V_{e,c-1}(x_c-x_{c-1}) = \dots = V_{e,2}(x_3-x_2) \\ &= V_{e,1}x_2 = 1 / \sum_{l=1}^{l=c} \frac{1}{V_{e,l}} \end{aligned}$$

for the rate with which chlorine atoms introduced in CCl_3 -skeleton by the reversal of C are flowing steadily in one direction from solution to chloroform. It follows that the latter rate is at least approximately given by the smallest one of these $V_{e,i}$'s.

**) The contribution is of course nil, if the hydrogen atom introduced in III is removed by any step prior to III.

to that of constituent chlorine atoms. If it did, however, the activity of the initial complex of III and hence its rate must be proportional to a certain power of the activity of chloride ion according to (8.6) in contradiction to the experimental result. The same experimental result excludes the possibility of any chloride ion similarly attached to the skeleton on the final complex III, since, if so, then the chloride ion must be included in its initial complex, it not attached to the skeleton; this leads to the same contradiction.

The skeleton must moreover keep the same number of protons attached to it as that of chloroform, when included in the initial complex of III of III_b(0)-type according to (iv) and Fig. 4, (III_b), as well as when included in its final complex, the step itself being a simple exchange of one proton. It follows that the constituent set of particles of the original chloroform molecule, and those of initial and final complexes of III are kept the same with each other throughout. Any two of them can not, however, be identical with each other according to (xi), in so far as III and at least one step ahead are kinetically significant. It follows now that we are dealing with at least three isomers, which is hardly conceivable for so simple a molecule as chloroform. Excluding this case, we now turn to the alternative one, when *Y* leads III in *Z*-series.

§ 10. Case when *Y* < III

It is similarly deduced as in the foregoing section that CCl₃-skeleton of chloroform is kept unchanged down to the initial complex of III. The foregoing step *Y* is, one of the types I(+1), II(0), III_a(0), III_b(+1) and III_a(+1) according to Fig. 3, Fig. 4 and to the foregoing section. Steps III_a(0)-, III_a(+1)- and III_b(+1)-type are excluded similarly as in the foregoing paper^{b)} on the ground of the appropriate k^{H^+}/k^{OH^-} -value.*)

I(+1) and II(0) are now two possible alternative types of *Y*. The initial complex of a step of I(+1)-type must be the bare skeleton as indicated by +1. There must then be at least one step preceding, which releases the proton of chloroform. The third isomer of chloroform is

*) Along with the assignment of *Y* to III_a(0)-type, we have to attribute its break at 3.2 pH to the point at which $k_{AB}=k^{OH^-}/a^{H^+}$ and the other break at which $k_{AB}=k^{H^+}a^{H^+}$ to pH lower than the lowest pH 0.1 of observation. It follows that $k_{AB}=k^{OH^-} \times 10^{3.2}$, $k_{AB} > k^{H^+} \times 10^{-0.1}$ and henceforth $\log_{10} k^{H^+}/k^{OH^-} < 3.3$ which is extremely lower than the range 11.1~7.6 deduced from the literature in the foregoing paper, or 10.4 obtained directly for III. III_a(+1)- and III_b(+1)-type are excluded just in the same way as III_a(0)-type is.

now obviated only by assigning the preceding step to the first step, Y to the second and III to the third, inasmuch as the initial complex of III must necessarily be an isomer of chloroform as deduced similarly as in the foregoing section.

Both the first and the second steps are now in equilibrium in the pH-region, where III determines the rate as concluded similarly to the argument in the foregoing section. The second step picks up a proton but it has nothing to do with hydrogen exchange between the original chloroform and solution, inasmuch as the intermediate in the final complex of the second step is that in the initial complex of III or is an isomer according to the above. It follows that the contribution to the observed hydrogen exchange is solely due to the first step. The latter being of type II(0), its rate $V_{e,z}$ varies with pH as II(0) Fig. 4.

The observed pH-dependence of Fig. 3 sufficiently verifies the statement that the hydrogen exchange is due to the first step.

We consider now the case when Y is of type II(0). The Y must be the first step of Z , in so far as the third isomer of chloroform is excluded in accordance with the above, and it, being of type II(0), must give rise to hydrogen exchange, whereas its contribution is $V_{e,y}$ at most.*^o As the observed rate of hydrogen exchange far exceeds the decomposition rate as shown in Fig. 3, it must be attributed to some other channel than the first step. Since the hydrogen exchange rate varies with pH as I(+1) or II(0) as observed, the channel must imply ionization of chloroform or of its isomer different from that leading to decomposition.

The latter isomer cannot be that implied in the initial complex of III, since hydrogen atom of chloroform is given up by Y before the isomer involved in III is formed and hence it contributes nothing to the observed hydrogen exchange. The above isomer of hydrogen exchange, if any, must be the third one.

Excluding the latter possibility in accordance with the above, the alternative is the ionization of the second kind of chloroform different from that leading to decomposition. We are now inevitably led to the possibility of the isomerism of CCl_3^- -ion, which is hardly conceivable any more than that of electronic configuration. Eliminating Y of type II(0) on this ground we are now left with that of type I(+1) alone.

*) The rate of hydrogen atom flowing into chloroform from solution or that of hydrogen exchange is the reverse rate of Y , which is equal to or extremely smaller than $V_{e,y}$ according to (5.5), (IX) and (i) in the respective cases when III or Y determines the rate.

The Mechanism of the Decomposition of Chloroform

Summing up, chloroform dissociates back and forth frequently in solution resulting in hydrogen exchange to keep up the step,



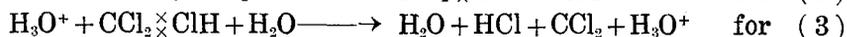
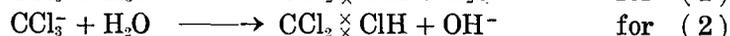
practically in equilibrium; CCl_3^- less frequently picks up a proton at Cl^- , instead of at C as in the reversal of the above step, to result in GEUTHER'S isomer $\text{HCl} \times \text{CCl}_2$ and the latter decomposes by simultaneous action of acid and base to give CCl_2 , which converts further through an unknown sequence of steps into the final product, the second and the third step alternately determining the rate at lower and higher pH respectively.

The correctness of the present conclusion depends on that of postulates (A), (B), (C) and that of the absence of the third isomer of chloroform and of the second one of CCl_3^- .

The conclusion to which we were led is apparently not very peculiar, although new in its foundation and kinetic presentation; the first step giving trichloromethyl anion is rather of general acceptance as discussed by HINE¹¹⁾ and the third one savours much of reappearance of GEUTHER'S old mechanism, chloroform of the structure suggested by him entering here as an isomer of the normal one well-established at present.

§ 12. Neutral Salt Effect

The mechanism enables us, in accordance with (8.4), to specify the steps respectively responsible for different parts of "Decomposition", (1), (2), (3) and (4) in Fig. 3 as,



and



It may readily be shown that values $\eta_{e,l}^{\text{SH}_2}$ of these steps are kept respectively constant independent of the neutral salt concentration at constant pH^{*)} remembering that η^{HCCl_3} is kept constant at the present

*) The $\eta_{e,l}^{\text{SH}_2}$ is associated with the condition that the steps preceding to l are all in equilibrium in accordance with (XI) and (6.5); $\eta_{e,3}^{\text{CCl}_3^-}$ is thus fixed according to (8.6) at $\eta^{\text{CCl}_2\text{H}}/\eta^{\text{H}^+}$ irrespective of the kind of acid involved in the preceding step (11.1), while $\eta_{e,3}^{\text{HCl} \times \text{CCl}_2}$ similarly at η^{HCCl_3} , suffix 2 or 3 referring respectively to step (11.2) or (11.3).

experimental condition by the presence of practically pure chloroform phase. The neutral salt effect hence comes into play only through the activity of the critical complex according to (8.5) in distinction from that in case of the well known neutral salt effect dealt with by BRÖNSTED.

We see immediately that the critical complex for (1) only is neutral, whereas those for all other parts are charged either positive or negative. This accounts for the experimental result that the neutral salt effect is present in all parts but (1) and that neutral salt depresses both (2) and (4) of negatively charged critical complex, while it exalts (3) of positively charged one, although we cannot see for the moment how the opposite sign of charge correlates with the opposite direction of the effect.

Summary

1. Decomposition of chloroform in contact with aqueous solution of different pH and neutral salt concentrations was followed in a sealed quartz vessel at 100°C in the absence of air by different methods *viz.*, observation of pH-variation due to decomposition product by means of BECKMAN pH-meter or pH-indicator, direct titration of liberated chloride ion by MOHR'S or VOLHARD'S method and colorimetry of ferric thiocyanate in the presence of mercuric thiocyanate and iron alum. The pH of the solution was adjusted by addition of sodium hydroxide or sulfuric acid or solid hydroxide of calcium or magnesium for retarding pH-variation due to decomposition and the neutral salt concentration was adjusted by addition of NaCl or Na₂SO₄.

2. The results of different observations of the decomposition rate were found consistent with each other and were in general features as follows; the decomposition rate V_a was (1) constant 5.0×10^{-7} mol/lit. min. from lowest pH 0.1 of observation up to pH 3.2, (2) increased from the latter point up to 3.2×10^{-6} at pH 4.0 with +1 inclination of $\log_{10} V_a$ against pH, (3) decreased from the maximum there down to 5.0×10^{-8} at pH 5.2 with nearly -1 inclination and then (4) increased from the minimum there steadily toward greater pH with inclination greater than +1 but tending to it gradually. The neutral salt effect on the decomposition rate was none in part (1) of the above-noted pH-dependence, depression in (2), exaltation in (3) and again depression in (4).

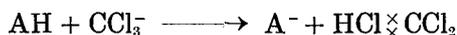
The Mechanism of the Decomposition of Chloroform

3. General theory of steady reaction was developed to deduce several rules on the basis of postulates, i. e., (A) a single chloroform molecule is converted by a series of consecutive steps through a sequence of intermediates into the decomposition product (B) the rate constant of each step and its reversal is independent of the activity of intermediate products and (C) the step involving proton transfer is one of three types,



where SH is the substrate, (chloroform or the intermediate), AH BRÖNSTED's acid, B base and S' an atom group into which that of S in SH is generally converted; AH was taken as H₂O or H₃O⁺ and B as OH⁻ or H₂O respectively exclusively.

4. The experimental results were then analysed by means of rules deduced in §8, incorporated with those of chlorine exchange in the foregoing paper⁵⁾ and of hydrogen exchange worked out by KANEKO and SATO both under the same conditions, presuming the absence of the third isomer of chloroform and of the second one of CCl₃⁻; the conclusion was that chloroform was converted through a sequence of steps,



into CCl₂, which was further decomposed to yield CO + 2HCl or H₂CO₂ + 2HCl through unknown steps; the first steps was responsible for hydrogen exchange and in cooperation with the second one, converted chloroform molecule into its isomer HCl × CCl₂, i. e., HCl combined with CCl₂ by coordinate bond; the second or the third step determined the rate over the region of pH respectively below or above that of the maximum at pH 4.0.

5. The observed neutral salt effect was adequately accounted for on the basis of the mechanism.

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