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HOMOGENEOUS HYDROGEN EXCHANGE BETWEEN CHLOROFORM AND HEAVY WATER

By

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Introduction

It is well-known that chloroform exchanges hydrogen with aqueous alkaline solution much more rapidly than it simultaneously decomposes1)2).

HINE, PEEK and OAKES2) have found that the rate of the exchange in alkaline solution is proportional to concentrations both of chloroform and hydroxide ion in the solution at 35°C. HORIUTI, TANABE and TANAKA3)4) observed the rate of chlorine exchange between aqueous solution and chloroform, and the rate of the decomposition at 100°C over the whole accessible pH-range keeping the solution saturated with coexistent phase of chloroform.

Present authors have determined, as reported below, the rate of hydrogen exchange over the pH-range from −1 to 10.5 at the similar experimental condition as that of the latter group of authors3)4) for deducing the mechanism of the respective reactions, incorporating results of these experiments3)4).

§ 1. Experimental

From 2 to 10 cc chloroform was sealed air-free together with from 1/2 to 2 cc heavy water solution with or without acidic or alkaline additions for adjusting pH, in a quartz tube of about 30 cc capacity, shaken briskly at 100°C, the quartz tube opened after a recorded time, about 1 cc chloroform pipetted out, dried over phosphorous pentoxide for about one day, burned at 800°C with copper oxide and the deuterium atomic fraction of the water thus formed was determined by means of micropyknometer5). Column X of Table 1 shows "Deuterium Fraction after Contact" x_t^c of chloroform thus found. The "Deuterium Fraction before Contact" x_0^s of the solution was determined as given in Column VI of

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TABLE 1 Specific Exchange Rate k^s of Hydrogen between Chloroform and Heavy Water at 100°C

No. of Runs	Aqueous Solution								Chloroform			Time of Contact t min	Specific Exchange Rate k^s mol/ℓ min
	Additions	pH		$[Cl^-]$ after Contact (calc.)	Deuterium Fraction			Volume v^s cc	Deuterium Fraction		Volume v^c cc		
		before Contact	after Contact (calc.)		before Contact $x_0^s \times 100$	after Contact $x_t^s \times 100$	at Equilibrium $x_\infty^s \times 100$		after Contact $x_t^c \times 100$	at Equilibrium $x_\infty^c \times 100$			
1	1.0gm Sat. $Ca(OH)_2$	10.6	10.0	0.28	22.15	·	·	2.0	3.21	17.69	2.0	2	0.991
2	0.5gm Sat. $Mg(OH)_2$	8.4	7.3	3.0×10^{-2}	22.30	·	·	2.0	5.08	17.04	3.0	180	2.80×10^{-2}
3	0.5gm Sat. $Mg(OH)_2$	8.4	7.3	3.0×10^{-2}	22.30	·	·	2.0	4.83	17.04	3.0	180	2.64×10^{-2}
4	0.5gm Sat. Ag_2O	8.65	7.4	5.2×10^{-3}	21.64	·	·	2.0	11.04	17.28	2.0	180	5.63×10^{-2}
5	None	6.2	1.8	1.4×10^{-2}	4.00	·	·	0.5	0.20	2.21	3.0	9300	3.8×10^{-4}
6	”	6.2	1.8	1.4×10^{-2}	4.00	·	·	0.5	0.10	2.21	3.0	9300	1.7×10^{-4}
7	”	6.2	3.3	4.6×10^{-4}	21.64	·	·	2.0	0.10	17.28	2.0	180	2.6×10^{-4}
8	0.00012 N HCl	3.92	3.3	5.5×10^{-4}	20.12	·	·	1.01	0.10	16.08	1.0	180	2.7×10^{-4}
9	0.24 N H_2SO_4	0.62	0.6	5.2×10^{-3}	4.00	·	·	0.5	0.09	2.21	3.0	3300	4.1×10^{-4}
10	0.25 N H_2SO_4	0.60	0.6	1.5×10^{-2}	4.00	·	·	0.5	0.26	2.21	3.0	9300	5.2×10^{-4}
11	1.4 N H_2SO_4	− 0.15	-0.1^5	1.9×10^{-2}	4.00	·	·	0.5	0.13	2.21	3.0	12000	1.8×10^{-4}
12	1.4 N H_2SO_4	− 0.15	-0.1^5	1.9×10^{-2}	4.00	·	·	0.5	0.29	2.21	3.0	12000	4.5×10^{-4}
13	6 N HCl	− 0.78	− 0.8	6.0	9.28	·	·	1.0	0.27	6.80	2.0	990	6.9×10^{-4}
14	6 N HCl	− 0.78	− 0.8	6.0	9.28	·	·	1.0	0.21	6.80	2.0	960	5.4×10^{-4}
15	0.44 N HCl	0.36	0.4	0.44	13.43	·	·	1.0	0.12	5.94	10.0	2150	4.4×10^{-4}
16	6 N HCl	− 0.78	− 0.8	6.0	9.28	9.25	7.75	1.0	·	·	2.0	990	4×10^{-4}
17	6 N HCl	− 0.78	− 0.8	6.0	9.28	9.24	7.75	1.0	·	·	2.0	960	5×10^{-4}
18	0.44 N HCl	0.36	0.4	0.44	13.43	13.38	12.23	1.0	·	·	1.0	2150	2×10^{-4}
I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV

Table 1 by measuring, with micropyknometer[5], the density of water distilled in vacuum from the solution frozen at −10°C to −30°C and then purified by several times of the similar distillations. In some Runs the reaction was followed alternatively by determining, quite similarly as x_0^s, the deuterium fraction x_t^s of the solution after contact as given in Column VII of Table 1.

Additions to heavy water for preparing heavy water solutions are, as shown in Column II of Table I, none for neutral solution, solid hydroxides of calcium, magnesium or silver, respectively of the quantities enough to keep the solution saturated with them for alkaline solutions and hydrochloric or sulphuric acid for acidic solution. The pH of solutions thus prepared or "pH before Contact" in Column III of Table 1 was determined as follows; that of neutral solution at 100°C was taken at 6.2, i.e. half the magnitude of $-\log K_h$, where

$$K_h = 48 \times 10^{-14} \quad (1)$$[6]

is the dissociation constant of water at 100°C, that of the acidic solution was identified with pH observed by means of glass electrode pH meter at room temperature and that of the alkaline solution was calculated as $\log_{10} 10n\, S/MK_h$, where S is the solubility of hydroxide added, in gm per 100 cc solution at 100°C given in Table 2, n the valency of hydroxide and M its molecular weight.

TABLE 2 Solubilities of Hydroxides gm/100 cc at 100°C[7]

Hydroxides	Ca $(OH)_2$	AgOH*)	Mg $(OH)_2$
Solubility	6.9×10^{-2}	3.1×10^{-3}	4.2×10^{-4}

*) Extrapolated from data given in Ref. 7 at lower temperatures.

The "pH after Contact" in Column IV and the appropriate value of $[Cl^-]$ in Column V of Table 1 were calculated from the "pH before Contact" and the observed rate of chloroform decomposition[4], as detailed in Appendix 1.

Chloroform used in the experiments was prepared just in the same way as in the previous works[3][4].

§ 2. Exchange Rate k^s of Hydrogen

The exchange rate of hydrogen was given by the specific rate k^s

of unidirectional deuterium transfer from solution to chloroform, determined from the above experimental results as follows. The increasing rate dx^c/dt of deuterium atomic fraction x^c in chloroform is given as

$$\frac{n^c}{v^s}\frac{dx^c}{dt} = k^s x^s - k^c x^c \,, \tag{2. a}$$

ignoring the simultaneous decomposition*) and admitting that the forward or backward rate, $k^s x^s$ or $k^c x^c$, per unit volume of heavy water solution is proportional to the momentary deuterium fraction x^s or x^c of solution or chloroform with proportionality constant k^s or k^c respectively, where n^c is the total gm atom of hydrogen, inclusive of protium and deuterium, comprised in chloroform, i. e. gm mol of chloroform present, v^s the volume of the solution and t the time of contact. Noting further the relation

$$n^s x^s + n^c x^c = n^D \,, \tag{2. b}$$

where n^s is the total gm atom of hydrogen in solution partaking the exchange reaction and n^D the constant total gm atom of deuterium in solution and in chloroform, we have from (2) by integration

$$\ln\frac{x^c_\infty - x^c_0}{x^c_\infty - x^c_t} = \ln\frac{x^s_0 - x^s_\infty}{x^s_t - x^s_\infty} = v^s(k^s/n^s + k^c/n^c)\,t\,, \tag{3. a}$$

where x^c_0 or x^s_0 is the value of x^c or x^s at $t=0$,

$$x^c_\infty = k^s n^D/(k^s n^c + k^c n^s) \tag{3. b}$$

and

$$x^s_\infty = k^c n^D/(k^s n^c + k^c n^s) \tag{3. c}$$

are the particular values respectively of x^c and x^s, which satisfy (2) at $dx^c/dt=0$, i. e. the equilibrium relation

$$x^c_\infty/x^s_\infty = k^s/k^c \equiv K\,. \tag{4}$$

The K is, as worked out statistical-mechanically in Appendix 3 for small deuterium abundance, given as

$$K = 0.877, \qquad 100^\circ\mathrm{C}. \tag{5}$$

The x^c_∞ or x^s_∞-values are shown in Column XI or VIII, Table 1 as calculated by (3.b) or (3.c) and (5) from n^c- or n^s-values derived from

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*) It is shown in Appendix 2, that both (2.a) and (3.a) remain practically valid even allowing for the decomposition of chloroform.

v^c or v^s given in Column XII or IX and from n^D calculated according to (2.b) as $n^D = n^s x_0^s + 2\times10^{-4} n^c$, taking x_0^c as the deuterium fraction of natural abundance 2×10^{-4}.

The k^s is now worked out by (3), (4) and (5), as given in Column XIV, Table 1.

§ 3. Results

The value of $\log_{10} k^s$ is plotted against pH as shown in Fig. 1. Those results, for which pH varies sensibly during the time of contact, are shown each by a segment of horizontal line at the height of $\log_{10} k^s$, with both its ends at pH before and after the contact marked off by vertical dashes.

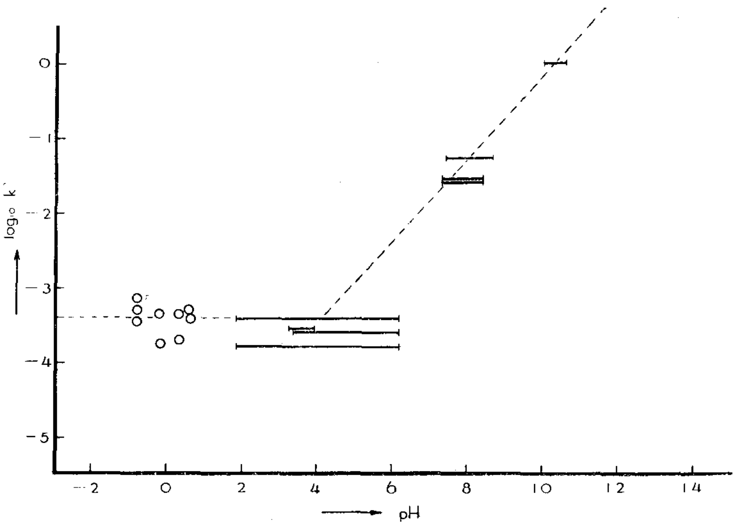

Fig. 1 Dependence of the specific exchange rate k^s of hydrogen on pH 100°C.

Fig. 1 shows that k^s runs, as indicated by dotted line, horizontally from pH = −1 up to *ca.* pH = 4 and increases from there on proportional to the hydroxide ion concentration in accordance with the results of HINE, PEEK and OAKES[2], providing an example of pH-variation of the rate controlled by a step of the type[4]

$$SH + B \longrightarrow S^- + H^+B,$$

where SH is a substrate of constant activity and B the BRÖNSTED's base, H_2O or OH^- exclusively. This result supports the mechanism of the exchange reaction[4,8,2], that it occurs through the elementary step

$$CHCl_3 + B \longrightarrow CCl_3^- + H^+B\,,$$

which is practically in equilibrium.

Summary

Deuterium exchange between deuterium shifted aqueous solution of pH from -1 to 10.5 and chloroform was followed at 100°C by shaking the aqueous solution and the coexistent phase of chloroform in vacuum, and by determining the deuterium content, after the recorded time of contact either of chloroform or of the aqueous solution. The specific rate k^s of the unidirectional deuterium transfer from aqueous solution to chloroform, i. e. the proportionality constant of the transfer rate to the product of the volume v^s and the deuterium atomic fraction x^s of aqueous solution was calculated from the result of the above observation by the equation

$$k^s v^s (1/n^s + 1/Kn^c)\,t = \ln \frac{x^c_\infty - x^c_0}{x^c_\infty - x^c_t} = \ln \frac{x^s_0 - x^s_\infty}{x^s_t - x^s_\infty}\,,$$

where n^s or n^c is the amount of hydrogen, inclusive both of protium and deuterium, in aqueous solution or in chloroform respectively, t the time of contact, x^s the deuterium atomic fraction of aqueous solution, suffix 0 or t or ∞ signifying the value of x^c and x^s before contact or after it or at the exchange equilibrium respectively, and $K = x^c_\infty / x^s_\infty$. The above equation was shown practically valid irrespective of the decomposition of chloroform concurrently occurring. The K was statistical-mechanically calculated from spectroscopic data and from the observation of exchange equilibrium between water and its vapour.

The specific rate k^s was thus found approximately to run flat from pH of -1 to *ca.* 4 rising from there on proportional to the hydroxide ion concentration. This result is in accord with the mechanism of the exchange reaction[4] attributed to the elementary step

$$CHCl_3 + B \longrightarrow CCl_3^- + H^+B$$

practically in equilibrium, where B is the base H_2O or OH^-.

The present authors wish to thank Prof. Juro HORIUTI for his kind help and valuable advices.

Appendix 1. Calculation of pH after Contact

The pH after contact is calculated as follows from that before and the observed rate of chloroform decomposition[4)] in the respective cases of different solutions used under the assumption that the activity coefficient of every solute is unity throughout.

Alkaline solution with addition of solid hydroxides. Electric neutrality of the solution requires that

$$n[\mathrm{Me}^{n+}]+[\mathrm{H}^+]=[\mathrm{OH}^-]+[\mathrm{Cl}^-]+[\mathrm{A}^-], \qquad \text{(i)}$$

where $[\mathrm{Me}^{n+}]$ is the concentration of metal ion Me^{n+} of hydroxide of valency n, $[\mathrm{A}^-]$ that of formate ion A^- produced from chloroform by decomposition and $[\mathrm{H}^+]$ etc. are concentrations of hydrogen ion H^+ etc. respectively. There exist relations among these concentrations, i.e.

$$K_s=[\mathrm{Me}^{n+}][\mathrm{OH}^-]^n,\ K_h=[\mathrm{H}^+][\mathrm{OH}^-],\ K_A=\frac{[\mathrm{A}^-][\mathrm{H}^+]}{[\mathrm{AH}]_u}, \quad \text{(ii.}s\text{)}, \text{(ii.}h\text{)}, \text{(ii.}A\text{)}$$

where K_s is the solubility product of hydroxide, K_h or K_A the dissociation constant of water or formic acid and $[\mathrm{AH}]_u$ the concentration of undissociated formic acid.

Denoting the sum $[\mathrm{A}^-]+[\mathrm{AH}]_u$ by the analytical concentration $[\mathrm{AH}]$ of formic acid as

$$[\mathrm{A}^-]+[\mathrm{AH}]_n=[\mathrm{AH}] \qquad \text{(iii)}$$

and the fraction of chloroform decomposed that produces formic acid, by α as

$$3[\mathrm{AH}]/[\mathrm{Cl}^-]\equiv\alpha^{*)}, \qquad (\text{iv}.\alpha)$$

we have by eliminating $[\mathrm{Me}^{n+}]$, $[\mathrm{OH}^-]$, $[\mathrm{A}^-]$, $[\mathrm{AH}]_n$ and $[\mathrm{AH}]$ from the above six equations

$$[\mathrm{Cl}^-]=\left(\frac{nK_s[\mathrm{H}^+]^n}{K_h^n}+[\mathrm{H}^+]-\frac{K_h}{[\mathrm{H}^+]}\right)\left(K_A+[\mathrm{H}^+]\right)\Big/\left\{\left(1+\frac{\alpha}{3}\right)K_A+[\mathrm{H}^+]\right\}$$
$$\equiv F\left([\mathrm{H}^+]\right), \qquad (\text{iv}.F)$$

Since $d[\mathrm{Cl}^-]/dt$ is given[4)] as a function $f([\mathrm{H}^+])$ of $[\mathrm{H}^+]$, i.e. as

$$d[\mathrm{Cl}^-]/dt=dF/dt=f([\mathrm{H}^+]) \qquad \text{(v)}$$

we have

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*) Three mols of hydrogen chloride are liberated per mol chloroform decomposed.

$$\int_0^t dF/f = t, \qquad \text{(vi)}$$

which enables us to determine $[\mathrm{H}^+]_t$ from $[\mathrm{H}^+]_0$, t and known functions $F([\mathrm{H}^+])$ and $f([\mathrm{H}^+])$.

Among constants in (iv.F), K_s was calculated from the solubility of hydroxides given in Table 2 as

$$K_s = n^n \left(\frac{10S}{M}\right)^{n+1}. \qquad \text{(vii.}s\text{)}$$

K_A was extrapolated at 100°C as

$$K_A = 1.1 \times 10^{-4} \qquad \text{(vii.}F\text{)}$$

from observations of HARNED and EMBREE9) at temperatures from 0° to 60°C and α taken as

$$\alpha = 0.1\ {}^{*)}, \qquad \text{(vii. }\alpha\text{)}$$

while K_h was given by (1).

The $f([\mathrm{H}^+])$ was picked up from data given in Fig. 1 of Ref. 4 as

TABLE 3 $f([\mathrm{H}^+]) \equiv d[\mathrm{Cl}^-]/dt$ mol ℓ^{-1} min^{-1}, 100°C

pH	0~3.3	3.6	4.0	4.5	5.0	5.5	5.8	6.0	6.5	7.0	7.5	8.0	8.5	9.0	9.5	10.0	10.5
$-\log f([\mathrm{H}^+])$	5.8	5.6	4.8	5.5	6.1	6.6	6.8	6.7	5.3	4.5	3.7	3.2	2.6	2.1	1.6	1.0	0.55

Eq. (iv.F) is written in this particular case, when $[\mathrm{H}^+]$ is negligible compared with K_A of (vii.F) as well as with $K_h/[\mathrm{H}^+]$, as

$$F \equiv \left(\frac{nK_s[\mathrm{H}^+]^n}{K_h^n} - \frac{K_h}{[\mathrm{H}^+]}\right) \Big/ \left(1 + \frac{\alpha}{3}\right). \qquad \text{(viii. }h\text{)}$$

The $[\mathrm{H}^+]_t$ is determined by adjusting it so as the area under the curve of $1/f$ plotted against F from $[\mathrm{H}^+]_0$ to $[\mathrm{H}^+]_t$ just gives the recorded time t of contact in accordance with (vi).

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*) According to J. HINE and T. B. LANGFORD α is 0.1 or less at 100°C. Actual calculation has shown that the allowance for the uppermost value 0.1 of α makes practically no difference in the calculated result of $[\mathrm{H}^+]_t$ in so far as the pH after contact is computed down to the first decimal place as in Column IV, Table 1. Authors' best thanks are due to Prof. J. HINE who afforded them, through the good offices of Prof. J. HORIUTI, to make use of the data in advance of publication.

Neutral and acidic solutions without sulfuric acid addition. Eq. (i) and hence (iv.F) hold in this case, but because of absence of solid hydroxide, (iv.F) is written here as

$$F \equiv \left([\mathrm{H}^+]-\frac{K_h}{[\mathrm{H}^+]}\right)\left(K_A+[\mathrm{H}^+]\right)\Big/\left\{\left(1+\frac{a}{3}\right)K_A+[\mathrm{H}^+]\right\}. \qquad \text{(viii. } a\text{)}$$

Acidic solution with sulfuric acid addition. Eq. (i) holds in this case by adding the normality $\frac{1}{2}[\mathrm{SO}_4^{--}]$ of sulfuric acid to its right hand side and (viii.a) does similarly by defining F as $F=\frac{1}{2}[\mathrm{SO}_4^{--}]+[\mathrm{Cl}^-]$ instead; $[\mathrm{Cl}^-]$ after contact is of course given by $F-\frac{1}{2}[\mathrm{SO}_4^{--}]$. The $[\mathrm{H}^+]_t$ and appropriate $[\mathrm{Cl}^-]$ are given quite similarly besides as in the foregoing two cases.

F- or $[\mathrm{Cl}^-]$- and appropriate pH-values thus determined are shown in Columns V and IV respectively of Table 1.

Appendix 2. Exchange Rate Allowed for the Concurrent Chloroform Decomposition

Eq. (2.a) is arrived at, even by taking the decomposition of chloroform into account, provided that the excess of the unidirectional rate of the backward transfer of deuterium from chloroform to solution over that of the forward one is given by $v^s V_d x^c$, where V_d is the rate of chloroform decomposition per unit volume of solution; for the rate $d(n^c x^c)/dt$ of deuterium increase in chloroform is then exactly given as

$$d(n^c x^c)/dt = v^s k^s x^s - v^s k^c x^c - v^s V_d x^c \ ,$$

which reduces to (2.a), since $-dn^c/dt = v^s V_d$ by definition.

Eq. (2) is integrated allowing for the variation of n^c, n^s and v^s as functions of time as follows. Eliminating x^s from (2), we have

$$dx^c/dt = v^s(k^c/n^c + k^s/n^s)(x^c_\infty - x^c) \ ,$$

where x^c_∞ is given according to (3.b) as a function of momentary values of n^c and n^s and hence of time; the integration gives

$$Xx^c_t = \int_0^t v^s(k^c/n^c + k^s/n^s)\, x^c_\infty X dt + x^c_0 \ , \qquad \text{(i. a)}$$

where

$$X = \exp\left(\int_0^t v^s(k^c/n^c + k^s/n^s)\,dt\right). \qquad \text{(i. b)}$$

Noting now that the differential $v^s(k^c/n^c+k^s/n^s)x^c_\infty X dt$ in (i.a) is written according to (i.b) as $x^c_\infty dX$, we have by partial integral of (i.a),

$$Xx^c_t = [x^c_\infty X]^t_0 - \int_0^t X dx^c_\infty + x^c_0\,,$$

i.e.,

$$X(x^c_{\infty,t} - x^c_t) = x^c_{\infty,0} - x^c_0 + \int_0^t X dx^c_\infty\,,$$

or by (i.b),

$$\ln\left(\frac{x^c_{\infty,0} - x^c_0}{x^c_{\infty,t} - x^c_t} + \varDelta\right) = \left(k^s\overline{v^s/n^s} + k^c\overline{v^s/n^c}\right)t = \ln X\,, \qquad \text{(ii. }X\text{)}$$

instead of (3.a), where $x^c_{\infty,t}$ or $x^c_{\infty,0}$ is the value of x^c_∞ at time t or 0 respectively and

$$\overline{v^s/n^s} = \frac{1}{t}\int_0^t\left(\frac{v^s}{n^s}\right)dt,\quad \overline{v^s/n^c} = \frac{1}{t}\int_0^t\left(\frac{v^s}{n^c}\right)dt,\quad \varDelta = \frac{\int_0^t X\,dx^c_\infty}{x^c_{\infty,t} - x^c_t}\,.$$

$$\text{(ii. }s\text{), (ii. }c\text{), (ii. }\varDelta\text{)}$$

The validity of (3.a) is now discussed with reference to the exact equation (ii.X). The upper bound to the decrease $-\varDelta n^c$ of n^c during the contact is given by $(d[\mathrm{Cl}^-]/dt)_m t/3$, where $(d[\mathrm{Cl}^-]/dt)_m$ is the greatest value of $d[\mathrm{Cl}^-]/dt$, given in Table 3 as a function of $[\mathrm{H}^+]$ during the contact. The upper bound amounts to 5×10^{-4} mol min^{-1} for Run 1, which is the greatest of those of all Runs, they being only of order of magnitude of 10^{-7} mol min^{-1} in neutral and acidic solution. Detailed calculation is carried out below with regard to Run 1.

Integral (vi) of Appendix 1 gives $f([\mathrm{H}^+])$ as a function of t and hence $[\mathrm{Cl}^-]$ is evaluated by the integral $\int_0^t f dt$. The decrease $-\varDelta n^c$ of n^c during the contact is now given as

$$-\varDelta n^c = v^s\frac{[\mathrm{Cl}^-]}{3} = \frac{v^s}{3}\int_0^t f\,dt = \begin{cases}1.86\times10^{-4}\text{ mol }(\alpha=0)\\ 1.84\times10^{-4}\text{ mol }(\alpha=0.1)\end{cases} \qquad \text{(iii)}$$

Eq. (iii) shows that $-\varDelta n^c$ is slightly suppressed for nonvanishing α in alkaline solution; this is to be attributed to the effect taken into account in (iv) of Appendix 1 that formic acid liberated reduces pH and in consequence the decomposition rate.

We infer further below first neglecting α. The appropriate amount of $-\Delta n^c$ is *ca.* 7 per mil of n^c, i. e.,

$$n^c = \frac{2\times 1.489}{119.4} = 0.0249 \text{ mol}, \qquad \text{(iv. } c\text{)}$$

where 1.489 or 119.4 is the density or the molecular weight of chloroform. We have on the other hand $\Delta n^s = -\Delta n^c$ in this case of $\alpha=0$, where Δn^s is the increment of n^s; Δn^s is now according to (iii) *ca.* 1 per mil of n^s, i. e.

$$n^s = 2\times \frac{2}{18} = 0.2222 \text{ mol}. \qquad \text{(iv. } s\text{)}$$

The increase of v^s in $\overline{v^s/n^c}$ or $\overline{v^s/n^s}$ due to the formation of hydrochloric acid is estimated as follows. The partial molal volume $\partial v^s/\partial n_i$ of a component i of the mixture is expessed as

$$\frac{\partial v^s}{\partial n^i} = \frac{M_i}{d}\left\{1+\frac{\partial \ln d}{\partial \ln(1-w_i)}\right\}^{*)}, \qquad \text{(v)}$$

where w_i or n_i is the weight fraction or the number of mols of component i, M_i its molecular weight and d the density of the mixture. Substituting d in (v) from the relation $d=1+w_i/2$ known empirically valid at room temperature for aqueous hydrochloric acid, we have

$$\frac{\partial v^s}{\partial n^i} = 18.2 \text{ c.c. mol}^{-1},$$

neglecting w_i or $2w_i$ of hydrochloric acid compared with 2 or 1 and putting $M_i=36.46$ and $d=1$. Assuming the latter equation valid approximately at 100°C, we have for the increment Δv^s of the solution, according to (iii),

$$\Delta v^s = 18.2\times 1.86\times 10^{-4}\times 3 = 0.010,$$

which is *ca.* 5 per mil of $v^s=2$ c.c.. As n^c decreases by 7 per mil and n^s increases by 1 per mil during the contact as shown above, v^s/n^c or v^s/n^s increases meanwhile 12 or 4 per mil respectively. The time mean $\overline{v^s/n^c}$ or $\overline{v^s/n^s}$ in (ii. X) exceeds in consequence from the respective initial value, of v^s/n^s or v^s/n^c by 12 or 3 per mil at most respectively.

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*) Expressing v^s by M/d, we have $\partial v^s/\partial n_i = M_i/d - M/d^2 \cdot \partial d/\partial n_i$, where M is the total mass of the solution and hence $\partial M/\partial n_i = M_i$. Since $w_i = M_i n_i/M$ by definition, we have $\partial w_i/\partial n_i = M_i/M - M_i n_i/M^2 \cdot \partial M/\partial n_i = M_i/M \cdot (1-w_i)$ or $\partial d/\partial n_i = \partial d/\partial w_i \cdot \partial w_i/\partial n_i = -M_i/M \cdot \partial d/\partial \ln(1-w_i)$ and hence (v).

Writing (ii.X) referring to (4) in the form

$$k^s = \frac{\ln\left(\dfrac{x^c_{\infty,0}-x^c_0}{x^c_{\infty,t}-x^c_t}+\Delta\right)}{t\left(\overline{v^s/n^s}+\dfrac{1}{K}\overline{v^s/n^c}\right)}, \tag{vi}$$

we see that the second term in the parentheses in the denominator is, according to (iv) and (5), $\frac{0.2222}{0.0249}\times\frac{1}{0.877}=10$ times as large as the first term there. The deviation of the second or the first term from the appropriate initial value being 12 or 4 per mil at most respectively, the error of k^s introduced by replacing the time mean by the appropriate initial value is practically 12 per mil at most, which is within a few percent errors associated with the experimental determination of the second term itself by pipetting chloroform or solution into the reaction tube with measuring pipette. The time mean is hence replaceable by the appropriate initial value without practically reducing the accuracy of k^s-determination.

We investigate now the error of k^s introduced by replacing the numerator of (vi) or the first member of (ii.X) with the first member of (3.a). We have according to (3.b) and (4), noting the relation $dn^s=-dn^c$, that

$$dx^c_\infty = \frac{Kn^D(1-K)}{(Kn^c+n^s)^2}\,dn^c, \tag{vii}$$

which assures according to (5) that dx^c_∞ is as well negative as dn^c is. X in (ii.Δ) increases steadily with time according to (i.b), whereas $x^c_{\infty,t}-x^c_t$ equals $n^s(k^s x^s-k^c x^c)/(k^s n^c+k^c n^s)$ by (3.b) and (2.b), which is positive according to (2.a), in so far as dx^c/dt is positive, in that situation we are interested. It follows now from (ii.Δ) that Δ is negative, that $\Delta>\frac{X\Delta x^c_\infty}{x^c_{\infty,t}-x^c_t}$, where X denotes its greatest value at t and hence from the first and the third member of (ii.X), that

$$\frac{x^c_{\infty,0}-x^c_0}{x^c_{\infty,t}-x^c_t}+\frac{X\Delta x^c_\infty}{x^c_{\infty,t}-x^c_t}<X \quad\text{or}\quad \frac{x^c_{\infty,0}-x^c_0}{x^c_{\infty,t}-x^c_t-\Delta x^c_\infty}<X,$$

noting that $x^c_{\infty,t}-x^c_t$ as well as $-\Delta x^c_\infty$ is positive. From the first and the third member of (ii.X) we have on the other hand because of negative Δ

$$\frac{x^c_{\infty,0}-x^c_0}{x^c_{\infty,t}-x^c_t}>X,$$

and in consequence

$$\frac{x^c_{\infty,0}-x^c_0}{x^c_{\infty,t}-x^c_t} > X > \frac{x^c_{\infty,0}-x^c_0}{x^c_{\infty,0}-x^c_t} ,$$

noting

$$\Delta x^c_\infty = x^c_{\infty,t}-x^c_{\infty,0} .$$

The Δx^c_∞ is now evaluated by (vii), (iv) and (2.b) identifying $\Delta x^c_\infty/\Delta n^c$ with dx^c_∞/dn^c on the ground that the variation (iii) of n^c and n^s of the magnitude of (iv) affects the coefficient of dn^c in (vii) quite insignificantly, as

$$\Delta x^c_\infty = \frac{0.877(0.2215n^s+0.0002n^c)\times 0.123\,\Delta n^c}{(0.877n^c+n^s)^2} = 0.0892\,\Delta n^c = -1.64\times 10^{-5} .$$

It follows that Δx^c_∞ lies quite within a few percent errors of $x^c_{\infty,0}$- or $x^c_{\infty,t}$-determination and hence we have

$$X = (x^c_\infty - x^c_0)/(x^c_\infty - x^c_t) , \tag{viii}$$

dropping the subscript 0 or t now shown practically insignificant.

It may be shown as below that the above conclusion is not altered, if we put $\alpha=0.1$ instead, assuming that hydrogen atoms attached to carbon atoms of formic acid are excluded from partaking the exchange reaction. Reserving notations n^s and n^c for the quantity of hydrogen atoms partaking the exchange reaction, and that n^D for the total quantity of deuterium excluded from partaking the exchange reaction or not, we have

$$x^s n^s - \alpha\Delta n^c x^{s'} + x^c n^c = n^D ,$$

$$x^c_\infty = K(n^D + \alpha\Delta n^c x^{s'})/(n^s + Kn^c) ,$$

$$n^s - \alpha\Delta n^c + n^c = n^s_0 + n^c_0 ,$$

instead respectively of (2.b), (3.b) and the relation $n^s+n^c=n^s_0+n^c_0$ valid in the case $\alpha=0$, where $x^{s'}$ is the deuterium atomic fraction in hydrogen atoms trapped by formic acid and in consequence $n_f \equiv -\alpha\Delta n^c x^{s'}$ is the quantity of deuterium thus trapped. Putting further approximately $dn_f = -\alpha x^c dn^c$, the quantity $K\{(1-K-\alpha)(x^s n^s + x^c n^c) + \alpha x^c(n^s + Kn^c)\}/(n^s + Kn^c)^2$ corresponding to the coefficient of dn^c in (vii) is evaluated and hence the above conclusion is invariably arrived at.

Eq. (3.a) holds now as follows from the second and third member of (ii.X), and (viii), inasumch as $\overline{v^s/n^s}$ or $\overline{v^s/n^c}$ is respectively replaceable, as shown above, by the appropriate initial value of v^s/n^s or v^s/n^c.

Practically exact validity of (3.a) has been admitted on the basis of the above result without the several control calculations for all other Runs, for which the calculated upper bound to $-\Delta n^c$ is far less than that of Run 1 as mentioned above.

Appendix 3. Evaluation of k^s/k^c

Let x^c_∞, x^s_∞, $x^c_\infty(g)$ and $x^s_\infty(g)$ be the deuterium atomic fractions of liquid chloroform, aqueous solution, chloroform vapour and water vapour respectively, which are in isotopic interchange equilibrium with each other. The K is expressed according to (4) as

$$K = x^c_\infty(g)/x^s_\infty(g)\,K_w\,, \qquad \text{(i. }k\text{)}$$

where

$$K_w = x^s_\infty/x^s_\infty(g) = 1.023^{10)\,*)}\,, \quad 100^\circ\mathrm{C}\,, \qquad \text{(i. }K\text{)}$$

identifying x^c_∞ with $x^c_\infty(g)$ on the ground that chloroform, as normal liquid, accommodates its hydrogen atom not much discriminatingly from that in its vapour compared with in the case of water, when hydrogen bond is formed particularly in the liquid state.

The raito $x^c_\infty(g)/x^s_\infty(g)$ in (i.k) is, at sufficiently low deuterium content is given as $[\mathrm{CDCl_3}]\ 2[\mathrm{H_2O}]/[\mathrm{CHCl_3}][\mathrm{HDO}]$, where $[\mathrm{CDCl_3}]$ etc. are concentrations of gas molecules $\mathrm{CDCl_3}$ etc. at interchange equilibrium and hence statistical-mechanically as

$$\frac{x^c_\infty(g)}{x^s_\infty(g)} = 2\,\frac{Q^{\mathrm{CDCl_3}}Q^{\mathrm{H_2O}}}{Q^{\mathrm{CHCl_3}}Q^{\mathrm{HDO}}}\,. \qquad \text{(ii)}$$

$Q^{\mathrm{CDCl_3}}$ etc. are partition functions of gas molecules $\mathrm{CDCl_3}$ etc. expressed by molecular constants of them represented by δ, as

$$Q^\delta = \frac{(2\pi m^\delta kT)^{3/2}}{h^3}\cdot\frac{8\pi^2}{\sigma(\delta)}\,\frac{(2\pi I^\delta kT)^{3/2}}{h^3}$$
$$\times\prod_{i=1}^{i=n(\delta)} 2\left[\sinh\frac{h\nu_i^\delta}{2kT}\right]^{-1}\exp\left(-\frac{\varepsilon_0^\delta}{kT}\right), \qquad \text{(iii)}$$

where m^δ is the mass of δ, I^δ the geometric mean of three principal moments of inertia, ν_i^δ the i-th vibrational frequency, ε_0^δ the lowest potential energy, $\sigma(\delta)$ the symmetry number, i.e. 1 or 2 for HDO or

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*) This value, observed with pure water, is identified with that with solutions in the present case.

H_2O and 3 both for $CHCl_3$ and $CDCl_3$ respectively, $n(\delta)$ the number of vibrational degrees of freedom of δ, i.e., 3 both for H_2O and HDO, and 9 both for $CHCl_3$ and $CDCl_3$, h or k the PLANCK's or BOLTZMANN's constant and T the absolute temperature.

TABLE 4 Molecular Constants

Molecules	I^{δ} (g. cm²)	Vibrational Frequencies w_i *) (cm⁻¹)						Anharmonic Constant $\frac{1}{4}\sum X_{j,k}$ (cm⁻¹)
$CHCl_3$	3.20×10^{-38}	3018.9	666.7	365.9	1215.6(2)	761.2(2)	260.5(2)	·
$CDCl_3$	3.24×10^{-38}	2256.0	650.8	366.5	908.3(2)	737.6(2)	262.0(2)	·
H_2O	1.80×10^{-40}	3825.3	1653.9	3935.6	·	·	·	− 76.1
HDO	2.55×10^{-40}	2820.3	1449.4	3883.8	·	·	·	− 56.8

*) Notation (2) annexed to the wave number means the two-fold degeneracy of the appropriate mode of vibration.

The $x_{\infty}^{c}(g)/x_{\infty}^{s}(g)$ is calculated by (ii) and (iii)*) on the base of molecular constants given in the Table 4, admitting that ε_0^{δ}'s remain unchanged by isotopic replacements, as

$$\frac{x_{\infty}^{c}(g)}{x_{\infty}^{s}(g)} = 0.8967. \qquad \text{(iv)}$$

We have (5) in the text from (iv) and (i).

References

1) J. HORIUTI and Y. SAKAMOTO, Bull. Chem. Soc. Japan **11**, 627 (1936).
2) J. HINE, R. C. PEEK, Jr. and B. D. OAKES. J. Am. Chem. Soc. **76**, 827, (1954).
3) J. HORIUTI, K. TANABE and K. TANAKA, Proc. Japan Acad. **27**, 404 (1951); this Journal **3**, 119 (1955).
4) J. HORIUTI, K. TANABE and K. TANAKA, this Journal **3**, 147 (1955).
5) E. S. GILFILLAN and M. POLANYI, Z. physik. Chem. A **166**, 254 (1933).
G. OKAMOTO and M. SHINDO, J. Chem. Soc. Japan **57**, 609 (1936).

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*) Anharmonic constant $1/4 \sum X_{jk}$ in Table 4 were taken into account in the case of water molecule only because of its large fundamental frequencies, and on the same ground the excited vibrational levels were ignored, replacing the harmonic approximation $\Pi\ 2\left(\sinh \frac{h\nu_i{}^{\delta}}{kT}\right)^{-1}$ of the vibrational partition function in (iii) with the BOLTZMANN factor of the ground vibrational level, i.e.,

$$\exp\left[-(\sum h\nu_i^{\delta}/2 + \sum X_{j.k}/4)/kT\right].$$

6) A. A. NOYES and Y. KATO, Landolt, "Tabellen", Hptw, II (1923) p. 1164.
7) A. SEIDELL, "Solubility of Inorganic and Metal Organic Compounds" 1940, New York.
8) S. SAKAMOTO, "Shokubai (Catalyst)" No. 5, 1 (1949).
9) H. S. HARNED and N. D. EMBREE, Landolt "Tabellen" Erg. III, c (1936), p. 2108.
10) M. IKUSIMA and S. AZAKAMI, J. Chem. Soc. Japan **59**, 40 (1938).