# THE REACTION BETWEEN BENZYL CHLORIDE AND WATER.

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The heterogeneous reaction which takes place at a liquid-liquid interface has been studied by several workers. In the majority of these cases, however, at least one of the reactants is solute molecules or ions dissolved in two immiscible solvents.

The object of the following experiments is to investigate the case where the immiscible liquids themselves react with each other at there interface. The reaction chosen as one of such cases was the hydrolysis of benzyl chloride by water according to the equation:

$$C_6H_5\cdot CH_2Cl + H_2O \rightarrow C_6H_5\cdot CH_2OH + HCl.$$

This reaction has been already studied by G. Harker,⁽¹⁾ who observed rather remarkable facts that benzyl chloride is not acted on by steam but decomposed by water with constant velocity. The present authors were interested to investigate the course of the reaction with water phase as well as vapour phase, of which only the former reaction is here published as they are obliged to interrupt the experiment. Since benzyl chloride is known to be practically insoluble in water, it will be sufficient to take only the surface reaction in consideration. In the present experiment a known volume of distilled water has been placed on the top of benzyl chloride, the former being stirred with constant rate, and the concentration of hydrochloric acid in it has been determined frequently at different intervals by measuring its electrical conductivity.

## Measurements.

A hard glass powder bottle of half liter capacity whose cross-sectional area is 40.0 sq. cm. was used as a reacton vessel. The vessel was closed with a cork stopper holding a thermometer (T), a platinum electrode (E), a small glass stirrer (S) and a fine glass tube (I), as is shown in Fig. 1, b. The two blades of the stirrer stand vertical so as not to disturb the interface of the two liquids.

A weighed quantity of 250 c.c. of distilled water is placed in the reaction vessel which is immersed right up to the neck in a water thermostat. On the other hand a pear shaped vessel (B) with a glass stopper, in which 50 c.c. of benzyl chloride (Schering-Kahlbaum's purest for scientific purposes) is placed, is also immersed in the thermostat. To the bottom opening of the above vessel (B) is connected a rubber tubing (R) with a rubber clip (P) and a glass tube (I), the latter being placed in the reaction vessel through the cork stopper. When the temperature becomes constant the pear shaped vessel (B) is somewhat lifted up and by opening the rubber clip (P) benzyl chloride is allowed to flow into the bottom of the reaction vessel. The tube (I) is then lifted slightly above the interface in order not to disturb it. The stirrer (S) is then started.

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The upper end of the stirrer rod is connected through a short rubber tubing (C) co-axial with a pivot of a wooden pulley, which is coupled with another wooden pulley fixed to the axis of a large stirrer of the thermostat. Since the thermostat-stirrer is driven by a small electric motor and regulated so as to rotate with constant rate (100 turns per min.), the rate of rotation of the glass stirrer in the reaction vessel can be controlled at will by choosing a pair of wooden pulleys having a suitable ratio of diameters.

The electrical conductivity of the aqueous layer was successively measured by means of a well calibrated Wheatstone's bridge with simultaneous record of time. The concentration of hydrochloric acid was calculated in mol/liter from the observed specific conductance by dividing it with the corresponding molecular conductance and multiplying with 1000. The viscosity of the reacted solutions was found to be identical with the hydrochloric acid solution of the same concentration and distilled water in the limits of the experimental errors.

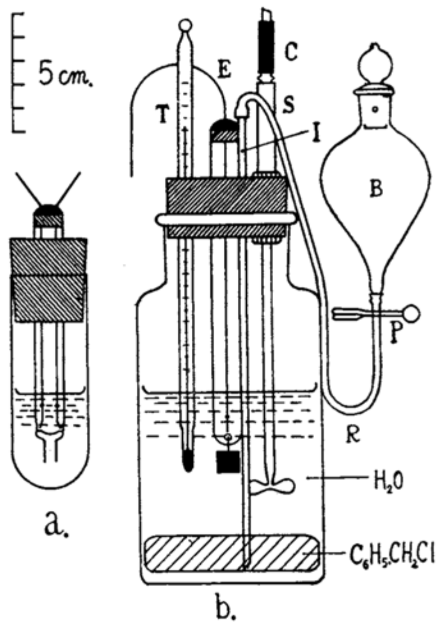

Fig. 1.

The necessary data of molecular conductance were determined by the writers at 30° and 50°C. The reaction vessel itself was used as a conductivity cell at 30°C., but as it required a considerable amount of solutions, a

30.0° C.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| $m$ | 0.000168 | 0.0002958 | 0.0005915 | 0.001183 | 0.005915 | 0.001183 | 0.05915 |
| $\Lambda$ | 450 | 449 | 447 | 450 | 448 | 441 | 423 |

50.0° C.

| | | | | | | |
|---|---|---|---|---|---|---|
| $m$ | 0.000333 | 0.000998 | 0.00333 | 0.00998 | 0.0333 | 0.0998 |
| $\Lambda$ | 570 | 570 | 570 | 560 | 540 | 506 |

small cell with the same electrode (shown in Fig. 1, a) was specially made for this purpose at 50°C. The values obtained are given in the following table, where $m$ expresses the concentration of hydrochloric acid in mol/liter and $\Lambda$ stands for the molecular conductance.

The conductivity measurement was started when the concentration of hydrochloric acid reached the lower limit of concentration in the control measurement of molecular conductance given above, namely $m = 0.000168$ at 30.0°C. and $m = 0.000333$ at 50.0°C. At first an experiment was done at 18°C. by using the molecular conductance data of Goodwin and Haskell,(1) but the rate of reaction at this temperature was so small that it required whole day to reach the limit just mentioned. All the other experiments, therefore, were carried out at 30° and 50°C., where this period varied from two hours to half an hour according to the temperature and the speed of stirring. Some of the results of the experiments are shown, as examples, by the curves in Figs. 2 and 3, where the figure on each curve indicates the number of revolution of the stirrer per minute. Full data will be given in later tables.

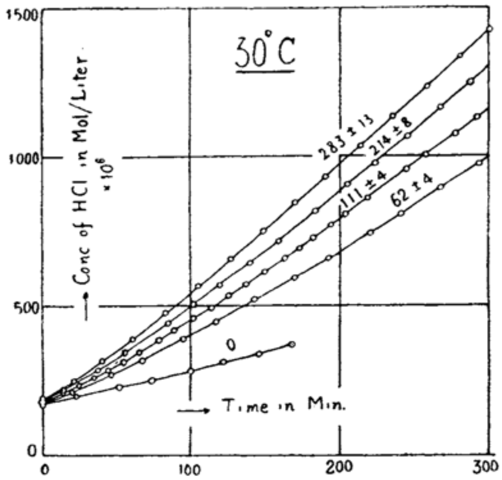

Fig. 2.

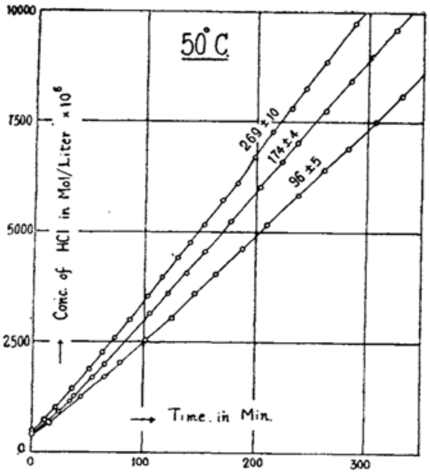

Fig. 3.

It will be seen from these curves that the rate of increase of hydrochloric acid is largely affected by the speed of stirring and, moreover, it increases with time, tending to become constant gradually.

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(1) *Phys. Rev.*, **19** (1904), 369.

## Results and Discussion.

The experimental results may be accounted for by assuming an adsorption film (A.F.) and a diffusion film (D.F.) in the aqueous part along the interface with benzyl chloride, as is shown in Fig. 4. These films may be movable as a whole but any configurations in the interior of them are supposed to be just like as on solid adsorbents.

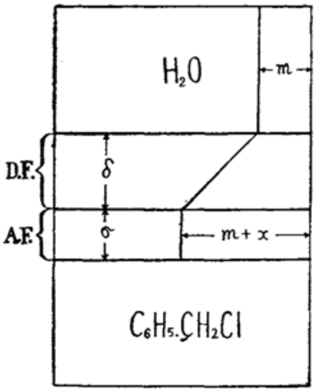

Fig. 4.

Since the reaction is a surface one and adsorbed molecules at the interface are supposed to hinder the progress of hydrolysis, its rate may be expressed by $H-kx$, where $x$ denotes the concentration of adsorbed molecules of hydrochloric acid, $H$ and $k$ being constants at a given temperature. Let $m$ express the concentration of hydrochloric acid in the bulk of aqueous layer whose volume is $V$, then the rate of increase of the total amount of hydrochloric acid in it is equal to $V\frac{dm}{dt}$, where $t$ denotes the time. The difference of the above two quantities may be equal to the rate of increase of hydrochloric acid in the adsorption film (A.F.), whose thickness is put as $\sigma$:

$$S\sigma\frac{d(m+x)}{dt} = H-kx-V\frac{dm}{dt}, \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

where $S$ denotes the area of the interface, $(m+x)$ being the actual concentration of hydrochloric acid in the adsorption film.

On the other hand, the rate of increase of hydrochloric acid in the bulk of the aqueous layer is equal to the amount which passes upwards in unit time through the diffusion film (D.F.). This amount is, however, proportional to the area of the interface $S$, the diffusion coefficient of hydrochloric acid $D$ in water and the concentration gradient in the diffusion film whose thickness is $\delta$:

$$V\frac{dm}{dt} = \frac{D\cdot S}{\delta}\left\{(m+x)-m\right\} = \frac{D\cdot S}{\delta}x. \quad \ldots\ldots\ldots\ldots \quad (2)$$

Solving this equation for $x$ and putting the result in equation (1) we have

$$S\sigma\frac{dx}{dt} = H-V\left(1+\frac{k\delta}{D\cdot S}+\frac{S\sigma}{V}\right)\frac{dm}{dt}. \quad \ldots\ldots\ldots\ldots \quad (3)$$

Differentiating equation (2) with regards to $t$ and substituting equation (3) in it we have

$$\frac{d^2m}{dt^2}+\frac{D}{\delta\sigma}\left(1+\frac{k\delta}{DS}+\frac{S\sigma}{V}\right)\frac{dm}{dt}=\frac{D}{\delta\sigma V}H. \quad \ldots\ldots\ldots\ldots \quad (4)$$

As the solution of this differential equation we obtain

$$\frac{dm}{dt}=A-Ce^{-Bt}, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (5)$$

where $C$ is an integration constant and

$$A=\frac{H}{V\left(1+\frac{k\delta}{DS}+\frac{S\sigma}{V}\right)}, \qquad B=\frac{D}{\delta\sigma}\left(1+\frac{k\delta}{DS}+\frac{S\sigma}{V}\right). \quad \ldots \quad (6)$$

But, since $\frac{S\sigma}{V}$ is very small compared with unity, equations (6) may be written in the form:

$$A=\frac{H}{V\left(1+\frac{k\delta}{DS}\right)}, \qquad B=\frac{D}{\delta\sigma}\left(1+\frac{k\delta}{DS}\right). \quad \ldots\ldots\ldots \quad (7)$$

The relation between $m$ and $t$ is obtained by integrating equation (5)

$$m=At+\frac{B}{C}e^{-Bt}+K, \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

where $K$ is an integration constant.

Equation (8) was tested by comparing the calculated values of $m$ with those observed. The results are very satisfactory as is shown in the following tables, in which $N$ denotes the number of revolution of the stirrer per minute. The constants in equation (8) were computed in the following manner: The value of $A$ which is equal to the reaction rate after sufficiently long time (cf. eq. (5)), can be directly known from the slope of the straight portion of the $t-m$ curve shown for example in Figs. 2 and 3. Then by plotting the value of log $(A—dm/dt)$ against the time $t$ we obtain a straight line (cf. eq. (5)), whose slope gives the value of $B$, $C$ being known from the point of the line on the abscissa.

### 18.0°C. $N = 109 \pm 2$*

$A = 1.00\times 10^{-6}$
$K = 978\times 10^{-6}$

| $t$ min. | $m\times\ 0^6$ (obs.) | $m\times 10^6$ (calc.) | $\Delta$ |
|---|---|---|---|
| 0 | 980.8 | 978 | −3 |
| 32 | 1014 | 1010 | −4 |
| 72 | 1047 | 1050 | +3 |
| 98 | 1071 | 1076 | +5 |
| 128 | 1109 | 1106 | −3 |
| 163 | 1144 | 1141 | −3 |
| 203 | 1179 | 1181 | +2 |
| 248 | 1225 | 1226 | +1 |

* Continued from the last day.

### 30.0°C. $N = 0$.

$A = 1.69\times 10^{-6}$, $B = 0.00352$,
$C = 0.689\times 10^{-6}$, $K = -22\times 10^{-6}$.

| $t$ min. | $m\times 10^6$ (obs.) | $m\times 10^6$ (calc.) | $\Delta$ |
|---|---|---|---|
| 0 | 170.7 | 173 | +2 |
| 23 | 199.3 | 197 | −2 |
| 52 | 230.2 | 229 | −1 |
| 74 | 251.3 | 254 | +3 |
| 100 | 285.4 | 284 | −1 |
| 122 | 313.1 | 311 | −2 |
| 146 | 340.3 | 342 | +2 |
| 168 | 370.2 | 370 | 0 |

### 30.0°C. $N = 62 \pm 2$.

$A = 3.90\times 10^{-6}$, $B = 0.00440$,
$C = 1.897\times 10^{-6}$, $K = -260\times 10^{-6}$,

| $t$ min. | $m\times 10^6$ (obs.) | $m\times 10^6$ (calc.) | $\Delta$ |
|---|---|---|---|
| 0 | 173.4 | 172 | −1 |
| 13 | 199.3 | 198 | −1 |
| 22 | 218.3 | 218 | 0 |
| 33 | 242.4 | 242 | 0 |
| 45 | 270.6 | 270 | −1 |
| 55 | 293.0 | 294 | +1 |
| 66 | 319.4 | 320 | +1 |
| 77 | 346.7 | 348 | +1 |
| 92 | 385.8 | 387 | +1 |
| 110 | 434.8 | 435 | 0 |
| 125 | 476.4 | 477 | +1 |
| 143 | 526.9 | 528 | +1 |
| 163 | 586.0 | 587 | +1 |
| 179 | 633.4 | 634 | +1 |
| 194 | 680.6 | 681 | 0 |
| 208 | 723.8 | 725 | +1 |
| 227 | 787.2 | 785 | −2 |
| 246 | 846.3 | 846 | 0 |
| 267 | 914.7 | 914 | −1 |
| 280 | 957.9 | 958 | 0 |

### 30.0°C. $N = 62 \pm 1$.

$A = 3.82\times 10^{-6}$, $B = 0.00440$,
$C = 1.910\times 10^{-6}$, $K = -260\times 10^{-6}$.

| $t$ min. | $m\times 10^6$ (obs.) | $m\times 10^6$ (calc.) | $\Delta$ |
|---|---|---|---|
| 0 | 175.3 | 175 | 0 |
| 20 | 213.2 | 214 | +1 |
| 47 | 270.6 | 273 | +2 |
| 68 | 318.6 | 322 | +3 |
| 95 | 391.4 | 389 | −2 |
| 117 | 447.3 | 447 | 0 |
| 143 | 521.8 | 518 | −4 |
| 170 | 595.5 | 596 | 0 |
| 192 | 661.8 | 661 | −1 |
| 220 | 743.4 | 745 | +2 |
| 241 | 805.7 | 811 | +5 |
| 268 | 893.7 | 898 | +4 |
| 294 | 975.0 | 982 | +7 |

### 30.0°C. $N = 60 \pm 2$.*

$A = 3.77 \times 10^{-6}$,
$K = 4219 \times 10^{-6}$.

| $t$ min. | $m \times 10^6$ (obs.) | $m \times 10^6$ (calc.) | Δ |
|---|---|---|---|
| 0 | 4215 | 4219 | + 4 |
| 18 | 4281 | 4287 | + 6 |
| 42 | 4383 | 4377 | − 6 |
| 66 | 4473 | 4468 | − 5 |
| 85 | 4528 | 4539 | +11 |
| 104 | 4624 | 4611 | −13 |
| 121 | 4663 | 4675 | +12 |
| 140 | 4764 | 4747 | −17 |
| 163 | 4848 | 4834 | −14 |
| 193 | 4936 | 4947 | +11 |
| 215 | 5050 | 5029 | −21 |
| 253 | 5145 | 5173 | +28 |
| 273 | 5243 | 5248 | + 5 |
| 295 | 5335 | 5331 | − 4 |
| 319 | 5425 | 5422 | − 3 |
| 346 | 5518 | 5523 | + 5 |

* Continued from (62±1) over a night.

### 30.0°C. $N = 101 \pm 5$.

$A = 4.01 \times 10^{-6}$, $B = 0.00449$,
$C = 1.845 \times 10^{-6}$, $K = -224 \times 10^{-6}$.

| $t$ min. | $m \times 10^6$ (obs.) | $m \times 10^6$ (calc.) | Δ |
|---|---|---|---|
| 0 | 186.4 | 187 | +1 |
| 17 | 224.5 | 225 | 0 |
| 36 | 269.2 | 270 | +1 |
| 55 | 314.9 | 318 | +3 |
| 73 | 361.7 | 366 | +4 |
| 92 | 421.5 | 417 | −5 |
| 111 | 476.4 | 471 | −5 |
| 137 | 553.5 | 548 | −6 |
| 154 | 598.8 | 600 | +1 |
| 171 | 656.1 | 653 | −3 |
| 188 | 706.0 | 707 | +1 |
| 206 | 765.2 | 765 | 0 |
| 224 | 823.9 | 824 | 0 |
| 241 | 876.6 | 881 | +4 |
| 262 | 946.2 | 953 | +7 |
| 281 | 1015 | 1018 | +3 |
| 304 | 1096 | 1100 | +4 |

### 30.0°C. $N = 111 \pm 4$.

$A = 4.03 \times 10^{-6}$, $B = 0.00640$,
$C = 1.688 \times 10^{-6}$, $K = -89 \times 10^{-6}$.

| $t$ min. | $m \times 10^6$ (obs.) | $m \times 10^6$ (calc.) | Δ |
|---|---|---|---|
| 0 | 176.7 | 175 | −2 |
| 14 | 210.7 | 209 | −2 |
| 25 | 236.2 | 237 | +1 |
| 35 | 260.9 | 263 | +2 |
| 45 | 288.3 | 290 | +2 |
| 55 | 313.1 | 317 | +4 |
| 66 | 347.5 | 350 | +2 |
| 79 | 387.2 | 388 | +1 |
| 89 | 416.7 | 419 | +2 |
| 102 | 457.6 | 459 | +1 |
| 114 | 493.6 | 497 | +3 |
| 126 | 534.6 | 537 | +2 |
| 137 | 573.1 | 573 | 0 |
| 150 | 617.0 | 616 | −1 |
| 163 | 660.1 | 661 | +1 |
| 173 | 693.6 | 695 | +1 |
| 182 | 728.6 | 726 | −3 |
| 194 | 770.5 | 769 | −2 |
| 204 | 805.7 | 805 | −1 |
| 219 | 860.2 | 859 | −1 |
| 245 | 956.1 | 953 | −3 |
| 258 | 1002 | 1002 | 0 |
| 278 | 1074 | 1076 | +2 |
| 292 | 1130 | 1129 | −1 |

### 30.0°C. $N = 161 \pm 5$.

$A = 4.15 \times 10^{-6}$, $B = 0.00972$,
$C = 1.852 \times 10^{-6}$, $K = -26 \times 10^{-6}$.

| $t$ min. | $m \times 10^6$ (obs.) | $m \times 10^6$ (calc.) | Δ |
|---|---|---|---|
| 0 | 165.0 | 165 | 0 |
| 20 | 212.8 | 211 | −2 |
| 43 | 277.4 | 278 | +1 |
| 64 | 340.3 | 342 | +2 |
| 83 | 401.4 | 403 | +2 |
| 107 | 485.7 | 485 | −1 |
| 142 | 608.8 | 611 | +2 |
| 163 | 685.8 | 689 | +3 |
| 181 | 757.9 | 758 | 0 |
| 202 | 840.4 | 839 | −1 |
| 225 | 928.5 | 929 | 0 |
| 247 | 1015 | 1016 | +1 |
| 267 | 1094 | 1096 | +2 |
| 288 | 1173 | 1171 | −2 |
| 310 | 1274 | 1269 | −5 |
| 333 | 1366 | 1364 | −2 |

30.0°C. $N = 209 \pm 3$.

$A = 4.36 \times 10^{-6}$, $B = 0.00979$,
$C = 1.709 \times 10^{-6}$, $K = -10 \times 10^{-6}$.

| $t$ min. | $m \times 10^6$ (obs.) | $m \times 10^6$ (calc.) | $\Delta$ |
|---|---|---|---|
| 0 | 166.5 | 166 | −1 |
| 11 | 195.7 | 196 | 0 |
| 22 | 228.3 | 228 | 0 |
| 31 | 254.9 | 255 | 0 |
| 45 | 297.8 | 299 | +1 |
| 56 | 332.0 | 336 | +4 |
| 71 | 388.6 | 388 | −1 |
| 84 | 434.8 | 434 | −1 |
| 99 | 489.2 | 489 | 0 |
| 110 | 532.0 | 530 | −2 |
| 123 | 579.2 | 579 | 0 |
| 134 | 620.4 | 622 | +2 |
| 146 | 667.4 | 670 | +3 |
| 169 | 764.2 | 765 | +1 |
| 180 | 806.9 | 806 | −1 |
| 192 | 858.8 | 855 | −4 |
| 206 | 913.1 | 912 | −1 |
| 220 | 969.8 | 970 | 0 |
| 231 | 1015 | 1016 | +1 |
| 246 | 1081 | 1080 | −1 |
| 261 | 1144 | 1143 | −1 |

30.0°C. $N = 214 \pm 8$.

$A = 4.31 \times 10^{-6}$, $B = 0.00921$,
$C = 1.796 \times 10^{-6}$, $K = -11 \times 10^{-6}$.

| $t$ min. | $m \times 10^6$ (obs.) | $m \times 10^6$ (calc.) | $\Delta$ |
|---|---|---|---|
| 0 | 184.5 | 184 | −1 |
| 14 | 220.5 | 220 | −1 |
| 38 | 288.3 | 290 | +2 |
| 56 | 346.7 | 346 | −1 |
| 85 | 441.9 | 442 | 0 |
| 102 | 505.0 | 505 | 0 |
| 120 | 569.0 | 571 | +2 |
| 140 | 644.6 | 646 | +1 |
| 159 | 718.1 | 719 | +1 |
| 184 | 817.7 | 818 | 0 |
| 205 | 904.1 | 903 | −1 |
| 224 | 978.4 | 979 | +1 |
| 246 | 1068 | 1069 | +1 |
| 268 | 1163 | 1161 | −2 |
| 288 | 1245 | 1244 | −1 |
| 305 | 1317 | 1316 | −1 |
| 325 | 1405 | 1400 | −5 |

30.0°C. $N = 283 \pm 13$.

$A = 4.55 \times 10^{-6}$, $B = 0.01117$,
$C = 1.514 \times 10^{-6}$, $K = 48 \times 10^{-6}$.

| $t$ min. | $m \times 10^6$ (obs.) | $m \times 10^6$ (calc.) | $\Delta$ |
|---|---|---|---|
| 0 | 187.3 | 190 | +3 |
| 21 | 250.2 | 249 | −1 |
| 41 | 316.7 | 313 | −4 |
| 61 | 391.4 | 387 | −4 |
| 83 | 476.4 | 472 | −4 |
| 105 | 567.8 | 568 | 0 |
| 127 | 660.1 | 657 | −3 |
| 149 | 750.6 | 750 | −1 |
| 170 | 842.9 | 845 | +2 |
| 190 | 930.3 | 931 | +1 |
| 214 | 1034 | 1034 | 0 |
| 236 | 1134 | 1141 | +7 |
| 259 | 1231 | 1228 | −3 |
| 281 | 1336 | 1340 | +4 |
| 301 | 1423 | 1423 | 0 |
| 325 | 1530 | 1529 | −1 |

30.0°C. $N = 283 \pm 3$.

$A = 4.50 \times 10^{-6}$, $B = 0.01117$,
$C = 2.084 \times 10^{-6}$, $K = -20 \times 10^{-6}$.

| $t$ min. | $m \times 10^6$ (obs.) | $m \times 10^6$ (calc.) | $\Delta$ |
|---|---|---|---|
| 0 | 166.0 | 167 | +1 |
| 11 | 194.8 | 195 | 0 |
| 23 | 230.7 | 228 | −3 |
| 35 | 264.1 | 264 | 0 |
| 48 | 304.4 | 304 | 0 |
| 60 | 346.7 | 346 | −1 |
| 72 | 391.4 | 388 | −3 |
| 84 | 433.1 | 431 | −2 |
| 96 | 476.4 | 476 | 0 |
| 108 | 521.8 | 522 | 0 |
| 121 | 573.7 | 573 | −1 |
| 135 | 628.3 | 628 | 0 |
| 151 | 690.9 | 695 | +4 |
| 166 | 756.8 | 756 | −1 |
| 182 | 822.6 | 824 | +1 |
| 198 | 890.8 | 892 | +1 |
| 213 | 956.1 | 956 | 0 |
| 235 | 1049 | 1052 | +3 |
| 253 | 1131 | 1129 | −2 |

### 50.0°C. $N = 96 \pm 5$.

$A = 24.31 \times 10^{-6}$, $B = 0.0237$,
$C = 8.792 \times 10^{-6}$, $K = 52 \times 10^{-6}$.

| $t$ min. | $m \times 10^6$ (obs.) | $m \times 10^6$ (calc.) | $\Delta$ |
|---|---|---|---|
| 0 | 425.1 | 423 | − 2 |
| 15 | 674.2 | 677 | + 3 |
| 44 | 1251 | 1253 | + 2 |
| 65 | 1706 | 1712 | + 6 |
| 79 | 2036 | 2029 | − 7 |
| 101 | 2539 | 2534 | − 5 |
| 125 | 3127 | 3110 | −17 |
| 145 | 3596 | 3589 | − 7 |
| 164 | 4040 | 4047 | + 7 |
| 188 | 4632 | 4627 | − 5 |
| 210 | 5164 | 5160 | − 4 |
| 238 | 5826 | 5839 | +13 |
| 261 | 6403 | 6397 | − 6 |
| 283 | 6923 | 6933 | +10 |
| 307 | 7508 | 7515 | + 7 |
| 331 | 8091 | 8098 | + 7 |
| 358 | 8754 | 8756 | + 2 |

### 50.0°C. $N = 174 \pm 4$.

$A = 29.53 \times 10^{-6}$, $B = 0.0283$,
$C = 11.00 \times 10^{-6}$, $K = 13 \times 10^{-6}$.

| $t$ min. | $m \times 10^6$ (obs.) | $m \times 10^6$ (calc.) | $\Delta$ |
|---|---|---|---|
| 0 | 401.4 | 401 | 0 |
| 14 | 688.2 | 687 | − 1 |
| 24 | 918.1 | 919 | + 1 |
| 38 | 1269 | 1267 | − 2 |
| 54 | 1692 | 1692 | 0 |
| 65 | 1998 | 1995 | − 3 |
| 105 | 3127 | 3134 | + 7 |
| 121 | 3596 | 3600 | + 4 |
| 138 | 4060 | 4059 | − 1 |
| 154 | 4559 | 4566 | + 7 |
| 177 | 5226 | 5234 | + 8 |
| 203 | 6012 | 6009 | − 3 |
| 223 | 6587 | 6600 | +13 |
| 237 | 7023 | 7012 | −11 |
| 262 | 7746 | 7750 | + 4 |
| 285 | 8433 | 8429 | − 4 |
| 304 | 8989 | 8991 | + 2 |
| 325 | 9614 | 9611 | − 3 |
| 348 | 10310 | 10293 | −17 |
| 370 | 11000 | 10943 | −57 |

### 50.0°C. $N = 269 \pm 10$.

$A = 33.64 \times 10^{-6}$, $B = 0.0279$,
$C = 12.42 \times 10^{-6}$, $K = 50 \times 10^{-6}$.

| $t$ min. | $m \times 10^6$ (obs.) | $m \times 10^6$ (calc.) | $\Delta$ |
|---|---|---|---|
| 0 | 493.2 | 496 | + 3 |
| 11 | 744.0 | 748 | + 4 |
| 21 | 1015 | 1005 | −10 |
| 36 | 1438 | 1424 | −14 |
| 51 | 1893 | 1874 | −19 |
| 63 | 2271 | 2246 | −25 |
| 74 | 2569 | 2596 | +27 |
| 87 | 2998 | 3016 | +18 |
| 103 | 3523 | 3540 | +17 |
| 116 | 3966 | 3971 | + 5 |
| 130 | 4420 | 4435 | +15 |
| 141 | 4760 | 4803 | +43 |
| 153 | 5164 | 5204 | +40 |

### 50.0°C. $N = 269 \pm 10$.

(Continued)

| $t$ min. | $m \times 10^6$ (obs.) | $m \times 10^6$ (calc.) | $\Delta$ |
|---|---|---|---|
| 170 | 5719 | 5773 | +54 |
| 183 | 6220 | 6210 | −10 |
| 198 | 6699 | 6714 | +15 |
| 214 | 7268 | 7250 | −18 |
| 231 | 7788 | 7822 | +34 |
| 244 | 8258 | 8260 | + 2 |
| 262 | 8880 | 8865 | −15 |
| 288 | 9743 | 9739 | − 4 |
| 316 | 10730 | 10680 | −50 |
| 337 | 11450 | 11390 | −60 |
| 359 | 12100 | 12130 | +30 |
| 383 | 13010 | 12940 | −70 |

Table of Constants.

| Temp. | $N$ | $A\times10^6$ | $B$ | $C\times10^6$ | $K\times10^6$ |
|---|---|---|---|---|---|
| 18.0°C. | 109± 2* | 100 | – | – | 978 |
| 30.0°C. | 0 | 1.69 | 0.00352 | 0.689 | –22 |
| | 62± 2 | 3.90 | 0.00440 | 1.897 | –260 |
| | 62± 1 | 3.82 | 0.00440 | 1.910 | –260 |
| | 60± 2* | 3.77 | – | – | 4219 |
| | 101± 5 | 4.01 | 0.00449 | 1.845 | –224 |
| | 111± 4 | 4.03 | 0.00640 | 1.688 | –89 |
| | 161± 5 | 4.15 | 0.00972 | 1.852 | –26 |
| | 209± 3 | 4.36 | 0.00979 | 1.709 | –10 |
| | 214± 8 | 4.31 | 0.00921 | 1.796 | –11 |
| | 283±13 | 4.55 | 0.01117 | 1.514 | 48 |
| | 283± 3 | 4.50 | 0.01117 | 2.084 | –20 |
| 50.0°C. | 96± 5 | 24.31 | 0.0237 | 8.792 | 52 |
| | 174± 4 | 29.53 | 0.0283 | 11.00 | 13 |
| | 269±10 | 33.64 | 0.0279 | 12.24 | 50 |

* After sufficiently long time.

It will be seen from the above tables that the values of $A$ and $B$ increase not only with rise of temperature but also with the speed of stirring. And, moreover, the effect of stirring on $A$ is more prominent at higher temperatures. On the contrary the same effect on $B$ decreases with rise of temperatures, showing a tendency that $B$ becomes independent of the speed of stirring at sufficiently high temperatures. These facts may be accounted for by equation (7) at least qualitatively, taking into considerations the fact that the constants $H$ and $k$ have a property of reaction coefficient and $\delta$, the thickness of the diffusion film, becomes smaller when the speed of stirring increases.

It is clear from the above data that the reaction is not of zero order as was mentioned by Harker. The reaction can be supposed quite naturally to be of constant velocity if we neglect the adsorption and assume the reaction to be completely irreversible. Nevertheless the result of experiments makes it necessary to assume the presence of an adsorption layer and the hindrance of reaction by adsorbed molecules.

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