XXIV. QUANTITATIVE RELATIONS IN CAPILLARY ANALYSIS.

By HANS SCHMIDT.

From the Bacteriological Department, Lister Institute.

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When a dispersed system is allowed to fall on filter- or blotting-paper or to rise up into a strip of such a paper, one observes that the dispersed phase remains behind the medium of dispersion, which is in most cases water. This phenomenon, which involves an increase in the concentration of the dispersed phase in the paper, can be used for the qualitative testing of the nature of the substance as has been shown by the capillary analytical experiments of Goppelsroeder [1909].

Holmgren [1908] tried to establish a formula, which gives a quantitative relation between the extents of the dispersion medium and the dispersed phase. He experimented with diluted acids, especially with hydrochloric acid, by allowing the latter to drop on blotting-paper. Using Congo-red as indicator, he was able to show how far the acid was spread over the paper compared with the water. If a good and homogeneous blotting-paper is used, the figure caused by the diffusion of the drop approaches a circle.

Holmgren supposed that the relation between the water-zone, the largest radius of which may be R , and the inner circle of radius r caused by the acid, is constant for each concentration, so that the quotient of two different concentrations is equal to the quotient of these relations. Therefore, as $[\pi R^2 - \pi r^2]$ is the surface of the water-ring, the following relation exists according to Holmgren :

$$\frac{C}{C_1} = \frac{\frac{r^2}{R^2 - r^2}}{\frac{r_1^2}{R_1^2 - r_1^2}} \dots\dots\dots(1).$$

If we signify by P that concentration for which

$$\frac{r_1^2}{R_1^2 - r_1^2} = 1,$$

the following equation results :

$$C = P \cdot \frac{r^2}{R^2 - r^2} \dots \dots \dots (2),$$

or

$$P = C \cdot \frac{R^2 - r^2}{r^2} \dots \dots \dots (3).$$

If, therefore, the concentration C and the radii of the circles produced on blotting-paper by any drop of the acid are known, P is determined from equation (3). Holmgren supposed P to be constant for the same paper and independent of the concentration. He called P the paper constant and was then able to determine any other concentration by the equation (2), but with the limitation that this method was not to be used except for very dilute solutions between 2.0 and 0.01 %. The results of Goppelsroeder's experiments, which give only the measurements of capillary height in strips of filter-paper, can also be treated by this formula of Holmgren, if instead of the height-measurements their squares are taken.

Skraup [1909, 1 and 2] and his co-workers were able to confirm the applicability of this formula for capillary-analysis. On examining the amount of free hydrochloric acid in the gastric juice by this method, I found [Schmidt, 1913] that the results obtained agreed very closely with those obtained by titration. Later some doubts arose in my mind as to the correctness of Holmgren's formula and occasioned me to undertake the following investigation.

TECHNIQUE OF EXPERIMENTS.

I experimented exclusively with hydrochloric acid, an exactly adjusted normal solution of which was taken as the basis for the following dilutions between 2.0 and 0.05 %. One drop of these solutions was allowed to fall on blotting-paper from a short distance. Much attention was paid to insure that the drop had always the same volume. With an ordinary pipette it was not possible to get the volumes of the drops as exact as was desirable. I therefore used the dropping surface of Traube's stalagmometer, which gives exactly equal drops, if the temperature be kept constant and the instrument be not allowed to deviate from the vertical position. Blotting-papers are much better fitted for capillary analysis than filter-paper, but they must not be too thick and must have a smooth surface and a most homogeneous structure. I obtained a series of different blotting-papers from the firm of C. Schleicher und Schüll, Düren i. Rheinland. The papers marked Nos. 123

and 117 proved to be specially suitable for my purpose. The papers were stained by floating them rapidly through an alcoholic solution of Congo-red (0.04 %) or methyl-orange (0.1 %). In order to prevent the water from evaporating or at least to reduce the evaporation to a minimum, as soon as the drop was absorbed the paper was placed between two glass plates and a weight laid on the plate to avoid any wrinkling. The plates were then put on a small frame under a glass globe, the interior of which was kept saturated with moisture by means of wetted filter-paper below. To neglect the evaporation leads to false conclusions. The radii were measured in millimetres by the use of transmitted or reflected light, and since the figures of the larger spots are mostly elliptical owing to the direction of the fibres in the structure of the paper, the main axes as well as two oblique axes were measured, so that the given result is the average of the measurement of 4 diameters. The number of figures examined to determine any single point is in most cases at least 4. The measurement took place after exactly one hour, the process having then practically reached a standstill. In reality one may sometimes observe an increase of the radii even after 24 hours, but the amount of it is too insignificant to be noted, especially if only one drop is taken.

Referring to dilutions of acid under 0.1 % the measurement must take place earlier than one hour especially when Congo-red is used, because the blue colour disappears after a certain time, owing to chemical action.

EXPERIMENTS.

The mass of one drop given by a stalagmometer at the temperature of 18–20° is indicated by a . If the drop consisted of distilled water, its weight was found to be 0.1160 gr., and if it consisted of HCl of a concentration between 2.0 and 0.05 %, I found the average weight of a drop 0.116 gr., the differences of the specific gravity in so highly diluted acids being so small that they can be neglected without introducing an error which exceeds the error of observation.

Therefore, putting the volume equal to the weight (in case of dilute HCl) I give a the value of 0.116 gr. Supposing m parts of hydrochloric acid to be present in the drop a , the concentration is given by $C = \frac{m}{a}$ by means of which m is easily calculated.

Under the above described conditions, a series of observations was made, of which the following may be reproduced :

TABLE I.

Paper No. 123. $a=0.116$ gr.

Indicator:		Congo-red						Methyl-orange			
Number of drops:		1 a		2 a		3 a		1 a		2 a	
HCl %	m	R	r	R	r	R	r	R	r	R	r
2.0	2.32	23.12	21.87	32	29.37	37.87	34.25	23.12	21.62	29.81	26.43
1.0	1.16	23.5	19.62	32.37	26.5	38.5	31.25	23.37	19.56	31.75	26
0.75	0.87	24	18.37	32.37	24.5	38.7	29.5	23.37	18	32	24.25
0.5	0.58	23.62	16.56	31.87	22.18	37.8	26.5	24	16.87	32.25	22.43
0.4	0.464	23.87	15.75	32.75	21.5	38.2	22.12 (?)	23.62	15.56	32.37	20.75
0.3	0.348	23.62	14.63	32.25	19.68	37.0	23.5	23.62	14.75	31.62	19.56
0.2	0.232	23.37	12.37	31.5	17.12	37.3	20.62	23.62	12.25	32.12	17.12
0.1	0.116	23.5	10	31.62	13.5	37.8	16.62	23.62	10.75	32	13.75
0.05	0.058	23.7	8.62	—	—	—	—	23.43	—	—	—
Means of R		23.48		32.09				23.53		31.74	

TABLE II.

Paper No. 117. $a=0.116$ gr. Indicator: Congo-red.

Number of drops:		1 a		2 a		3 a	
HCl %	m	R	r	R	r	R	r
1.0	1.16	26.5	24.25	36.0	32.41	42.25	37.5
0.75	0.87	26.85	22.40	35.75	30.1	42.5	35.5
0.5	0.58	26.68	20.62	35.43	27.75	41.62	33.18
0.4	0.464	26.87	20.5	35.43	27.5	43	33.0
0.3	0.348	25.87	18.85	35.87	25.2	42.37	30.3
0.2	0.232	26.25	16.37	36.0	22.81	42.0	26.75
0.1	0.116	26.25	13.63	35.75	18.5	42.25	22.75
0.05	0.058	26.75	—	—	—	—	—
Means of R		26.50		35.75		42.28	

TABLE III.

Paper No. 123. $a=0.0311$ gr.

Indicator:		Congo-red		Methyl-orange	
HCl %	m	R	r	R	r
1.0	0.311	14.75	13.29	—	—
0.5	0.155	15.1	12.5	12.5	9.3
0.4	0.124	14.65	9.4	12.8	8.9
0.3	0.0933	14.84	8.85	12.7	8.25
0.2	0.0622	15.15	7.95	12.8	7
0.182	0.0566	13.3	6.4	12.9	6.36
0.1	0.0311	14.26	6.0	13.1	6
Means of R		14.6		12.8	

On the assumption that the aggregation of acid in the inner circle is of the nature of an adsorption process, the relationship between the two variables m and r must be expressible by the exponential equation

$$r = \beta m^p.$$

It is highly probable also that the concentration of the acid or that of the hydrogen ions is continuously decreasing from the centre to the periphery of the spot-system in the case of any drop of a certain concentration falling on the paper. I suppose then, that r indicates that point of hydrogen ion concentration which corresponds with the sensibility of the indicator. But owing to the impossibility of proving experimentally the gradual decrease of the hydrogen ion concentration in the paper between the centre and r , my supposition remains an hypothesis. To show how in different concentrations the relation between m and r is expressible by the equation $r = \beta m^p$, we use the graphic method in constructing the m - r -curve Fig. 1.

Fig. 1.

The m - r -curve rises very steeply in the beginning and then runs nearly parallel to the m -axis, asymptotically approaching a straight line, of which the equation is $r = R$. The difference $(R - r)$ is identical with the breadth of the water-zone and the latter is of course equal to R in case of distilled water, when m or $C = 0$. $(R - r)$ decreases with increase in the amount of m . Theoretically, the decrease of $(R - r)$ is infinite but in reality m reaches very soon such an amount, that the water-zone is no longer visible. When the latter effect occurs with one drop, the phenomenon can still be obtained by increasing the volume of the drop or augmenting the number of drops, but the errors of observation are also increasing and in such a

degree that for concentrations higher than 2.0% the method of Goppelsroeder is preferable, which, as already mentioned, involves the measurement of the capillary height in strips of filter-paper.

That R is in reality the constant, which it seems to be in the experimental data, and that R depends—in the same paper—only upon the volume of the drop and not upon the concentration, will be shown later.

By taking the logs. of the equation $r = \beta \cdot m^p$, we get

$$\log r = p \cdot \log m + \log \beta.$$

This is the equation of a straight line, which is very nearly approached by plotting the values of $\log r$ and $\log m$, as is shown in Fig. 2.

Fig. 2.

By graphic interpolation according to Freundlich's [1907] procedure the values of β and p are found to be

$$p = 0.264$$

and

$$\beta = 18.75.$$

In the following table the values are calculated by the equation

$$r = 18.75m^{0.264} \dots\dots\dots(4).$$

TABLE IV.

Paper 123. Congo-red. 1 drop ($a = 0.116$ gr.). $r = 18.75m^{0.264}$.

$C = \% \text{ HCl}$	m	r calculated	r observed	Δ calc. - obs.
2.0	2.32	23.41	21.87	- 1.54
1.0	1.16	19.49	19.62	+ 0.13
0.75	0.87	18.08	18.37	+ 0.29
0.5	0.58	16.31	16.56	+ 0.15
0.4	0.464	15.12	15.75	+ 0.63
0.3	0.348	14.19	14.63	+ 0.44
0.2	0.232	12.74	12.37	- 0.37
0.1	0.116	10.61	10	- 0.61
0.05	0.058	8.84	8.62	- 0.22

Although the agreement is fairly good, a further calculation of β and p was made by the following procedure in order to diminish the differences.

HCl %	$100 \times m$	$100 \times r$	$\log m$	$\log r$
2.0	232	2187	2.36549	3.33985
1.0	116	1962	2.06446	3.29248
0.75	87	1837	1.93952	3.26411
0.5	58	1656	1.77085	3.21906
0.4	46.4	1575	1.64652	3.19728
0.3	34.8	1463	1.54158	3.16524
0.2	23.2	1237	1.36549	3.09237
0.1	11.6	1000	1.06446	3
0.05	5.8	862	0.76343	2.93551
Mean			1.613533	3.167322

Deviations from means :

m_1	r_1	$m_1 \cdot r_1$	$(m_1)^2$
+0.75195	+0.172528	0.12957	0.56543
+0.45092	+0.125158	0.056432	0.20333
+0.32598	+0.096788	0.031551	0.051067
+0.15731	+0.051738	0.0081424	0.024746
+0.032987	+0.029958	0.00098825	0.0010881
-0.071953	-0.002082	0.000149806	0.0051772
-0.248043	-0.054952	0.013630	0.061523
-0.549073	-0.167322	0.091871	0.30147
-0.850103	-0.231812	0.19705	0.72267

$$P = \frac{\Sigma(m_1 \cdot r_1)}{\Sigma(m_1)^2} = \frac{0.529384}{1.9365013} = 0.2733.$$

The value 0.273 for the exponent p gives the following values for

$$\log \beta_1 = \log r - 0.273 \log m.$$

$\log \beta_1$	and for β_1
2.694072	494.4
2.728883	535.6
2.73462	542.7
2.73561	544.0
2.74778	559.4
-2.74438	555.1
2.711959	524.3
2.70940	512.1
2.72709	533.4

As the figures for r and m have been multiplied by 100, the values of $\log \beta$ in the equation

$$r = \beta \cdot m^p$$

are calculated from the following equation :

$$\log \beta = \log \beta_1 + 2 \cdot (0.273) - 2.$$

These values of $\log \beta$ are therefore the following :

$\log \beta$	β
1.25007	17.78
1.27488	18.83
1.28062	19.08
1.28161	19.12
1.29378	19.66
1.29038	19.51
1.26559	18.43
1.25540	18.00
1.27309	18.75

Mean of β 18.88

It results therefore for the relation between r and m the equation

$$r = 18.88 \cdot m^{0.273} \dots\dots\dots(5).$$

Thus substituting the calculated values for β and p the following equation was obtained:

$$r = 18.88 \cdot m^{0.273},$$

which gives a far better agreement between calculation and observation, as is shown in the following table:

TABLE V.

Paper 123. Indicator: Congo-red. One drop. $a=0.116$ gr. $r=18.88 \cdot m^{0.273}$.				
$C=\%$ HCl	m	r calculated	r observed	Δ
2.0	2.32	23.75	21.87	-1.88
1.0	1.16	19.66	19.62	-0.04
0.75	0.87	18.17	18.37	+0.2
0.5	0.58	16.34	16.56	+0.22
0.4	0.464	15.11	15.75	+0.64
0.3	0.348	14.15	14.63	+0.48
0.2	0.232	12.67	12.37	-0.3
0.1	0.116	10.48	10.0	-0.48
0.05	0.058	8.677	8.62	-0.05
Idem, but $a=0.0311$ gr.				
1.0	0.311	13.72	13.29	-0.43
0.5	0.155	11.09	12.5	+1.41
0.4	0.124	10.67	9.4	-1.27
0.3	0.0933	9.880	8.85	-1.03
0.2	0.0622	8.845	7.95	-0.89
0.182	0.0566	8.620	6.4	-2.42
0.1	0.0311	7.320	6	-1.32

The reason why the second part of the Table V does not show so good an agreement is the inexact measurement of drops by using an ordinary pipette instead of a stalagmometer. By increasing the number of drops, so that instead of a , $2a$ or $3a$ were taken of the same concentration $C=\frac{m}{a}$, the radii of the corresponding spots must be

$$r\sqrt{2}, \quad r\sqrt{3},$$

or, generally speaking, if $[na]$ is taken as the dropping mass, the corresponding

radius is $r\sqrt{n}$, r being the radius for a . Therefore, if the radii found for a are supposed to be fixed, the radii for $2a$ or $3a$ can be calculated. The following table gives the results:

TABLE VI.

Paper 123. Indicator: Congo-red. $a=0.116$ gr.

Number of drops: a		$2a$		$3a$	
$C=\%$ HCl	r_1	r_2 calculated	r_2 observed	r_3 calculated	r_3 observed
2.0	21.87	30.83	29.375	37.63	34.25
1.0	19.62	27.66	26.5	33.98	31.25
0.75	18.37	25.90	24.5	31.81	29.5
0.5	16.56	23.34	22.185	28.68	26.5
0.4	15.75	22.20	21.5	27.27	22.125 (?)
0.3	14.63	20.63	19.685	25.33	23.5
0.2	12.37	17.44	17.125	21.42	20.625
0.1	10.0	14.14	13.5	17.32	16.625
0.05	8.62	—	—	—	—

The agreement between the calculated and observed values for r is still fairly good for $2a$. But by increasing the number of drops beyond 2, the experimental error increases, because the figure produced on paper loses the resemblance to a circle, so that the average of r is determined with more arbitrariness. By using the equation (5)

$$r = 18.88 \cdot m^{0.273}$$

for cases where, generally speaking, (na) was taken, m becomes (nm) . The values of r_2 for $2m$ and of r_3 for $3m$ are shown in the following table:

TABLE VII.

Paper No. 123. Indicator: Congo-red. $a=0.116$ gr. $r_1\sqrt{n}=18.88 (nm)^{0.273}$.

$C=\%$ HCl	$2m$	$\log 2m$	r_2 calculated	r_2 observed	Δ observed - calc.	Δr_2 calculated - $r_2=r_1\sqrt{2}$
2.0	4.64	0.66652	28.71	29.37	+0.66	-2.12
1.0	2.32	0.36549	23.75	26.5	+3.25	-3.91
0.75	1.74	0.24055	21.96	24.5	+2.54	-3.94
0.5	1.16	0.06446	19.66	22.18	+2.52	-3.68
0.4	0.928	0.96755 - 1	18.38	21.5	+3.12	-3.82
0.3	0.696	0.84261 - 1	17.10	19.68	+2.58	-3.53
0.2	0.464	0.66652 - 1	15.31	17.12	+1.81	-2.13
0.1	0.232	0.36549 - 1	12.67	13.5	+0.83	-1.47

$C=\%$ HCl	$3m$	$\log 3m$	r_3 calculated	r_3 observed	Δ observed - calc.	Δr_3 calculated - $r_3=r_1\sqrt{3}$
2.0	6.96	0.84261	32.06	34.25	+2.09	-5.57
1.0	3.48	0.54158	26.53	31.25	+4.72	-7.45
0.75	2.61	0.41664	24.53	29.5	+4.97	-7.28
0.5	1.74	0.24055	21.96	26.5	+4.54	-6.72
0.4	1.392	0.13364	20.53	22.12 (?)	+1.59 (?)	-6.74
0.3	1.044	0.01870	19.10	23.5	+4.4	-6.23
0.2	0.696	0.84261 - 1	17.10	20.62	+3.52	-4.32
0.1	0.348	0.54158 - 1	14.15	16.62	+2.47	-3.17

The deviations of the calculated figures of r from those obtained by observation are so considerable as to make it clear that the volume used for capillary-analytic purposes must not exceed a certain quantity. But the deviation of the calculated values $r_1 \sqrt{n}$ and $18.88m^{0.273}$ must be due to the inexactness of the constant in the equation $r = \beta m^p$ and to the experimental errors for r_1 . In reality the relation

$$r_1 \sqrt{n} = \beta (n \cdot m^p) \dots\dots\dots(6)$$

must exist.

THEORETICAL PART.

On detailed consideration of the processes taking place in the paper, it becomes evident that an increase of concentration of the hydrochloric acid has taken place.

If C signify the original concentration and C_1 the resulting concentration in the coloured spot, the relation between these concentrations may be deduced in the following way. The paper is supposed to be previously stained either with 0.04% alcoholic Congo-red solution, or with 0.1% alcoholic methyl-orange solution, and the staining to be done in the same manner, the paper not being allowed to adsorb much of the dye, a process which is at room temperature only a matter of time, as has been shown by W. M. Bayliss [1906]. Observation shows that stained paper differs slightly in quality from unstained, a fact to which reference will be made later.

Let $[a]$ be the constant quantity of the drop and $[na]$ the quantity of hydrochloric acid of the concentration $C = \frac{m}{a}$, dropping on a piece of blotting-paper which is supposed to be always of the same quality. The quantity $[na]$ of the acid may spread over the paper, so that the acid reaches from the centre to the distance $r \sqrt{n}$, and the largest radius of the water-zone may be $R \sqrt{n}$, if r and R are the corresponding values for $[a]$. In case of another drop-volume, the weight being g' , the radius becomes $r \sqrt{\frac{g'}{g}}$, g being 0.116 gr.

As the acid constituent of $[na]$ is in the interstices of the paper, the volume $[na]$ must be equal to the volume of the paper, the air being included, minus the specific volume of the paper-material itself in the same space. The volume occupied by $[na]$ is $\pi n R^2$ and the specific volume of the paper-material is its weight divided by its specific gravity s . The weight of a portion of paper of square millimetre surface and thickness δ is indicated by p . Therefore the following equation results for $[na]$:

$$na = \pi n R^2 \delta - \pi n R^2 \frac{p}{s} \dots\dots\dots(7),$$

or, if $n = 1$,

$$a = R^2 \cdot \pi \left(\delta - \frac{p}{s} \right).$$

$\pi \left(\delta - \frac{p}{s} \right)$ represents a constant characteristic for the paper and may be indicated by k , so that

$$k = \pi \cdot \left(\delta - \frac{p}{s} \right)$$

and

$$a = R^2 \cdot k,$$

or

$$R = \sqrt{\frac{a}{k}} \dots \dots \dots (8).$$

That is to say, R depends only upon the variation in quality of the paper and upon the drop-volume which is taken, but it is independent of the concentration C . Therefore R is to be considered as constant for all concentrations, if the same paper and the same drop-volume are used.

The easiest and quickest way to find k is by means of the equation (8), but by weighing the paper and determining its specific gravity and thickness the same value for k will be obtained by the equation $k = \pi \cdot \left(\delta - \frac{p}{s} \right)$.

In order to determine the thickness δ of the paper, a certain number of sheets are placed between two glass plates and by pressing them very tightly the measure of the distance may be found, which gives when divided by the number of sheets a rough value of δ . The best manner to determine the specific gravities is the use of a pyknometer. The following data were thus obtained:

Paper No. 123	$\delta = 0.17$ mm. $p = 0.1408$ mgr. $s = 1.36$ $k = 0.20923$
Paper No. 117	$\delta = 0.16$ mm. $p = 0.118$ mgr. $s = 1.1$ $k = 0.1651$

When the value of k is found in this way, R can be calculated by the equation (8) as is shown in the following table:

TABLE VIII.

Paper No.	a (mgr.)	R calculated			R observed		
		a	$2a$	$3a$	a	$2a$	$3a$
123	116	23.537	33.28	40.77	23.48	32.09	37.9
117	116	26.49	37.48	45.90	26.5	35.75	42.28
123	13.1	12.165	—	—	12.8 Methyl-orange	—	—
					14.6 Congo-red		

The agreement is very close for a , but here, too, it is apparent that increase of the number of drops increases the inexactness of the observations. If the value of R_1 is fixed, R_2 and R_3 can be calculated as $R_1 \sqrt{2}$ and $R_1 \sqrt{3}$, which give also a fairly good agreement, as the following figures demonstrate:

TABLE IX.

Paper No.	a (mgr.)	R_1	$R_2 = R_1 \sqrt{2}$	$R_3 = R_1 \sqrt{3}$
123	116	23.5	33.13	40.70
117	116	26.5	37.36	45.89

If $C = \frac{m}{a}$, the quantity na of HCl contains nm parts of it. These nm parts of HCl have been retained by adsorption in the inner circle (r), and if v indicates the volume of its interstices, the following equation must express the resulting concentration C_1 :

$$C_1 = \frac{n \cdot m}{v}.$$

I neglect the possibility, that the fibres may swell, supposing that the adsorption process is much sooner finished than the swelling of the fibres.

By analogy with equation (7), v can be expressed by

$$v = \pi n r^2 \delta - \pi n r^2 \cdot \frac{p}{s}.$$

After substituting this value for v , C_1 is given by

$$C_1 = \frac{n \cdot m}{n r^2 \pi \cdot \left(\delta - \frac{p}{s} \right)},$$

or

$$C_1 = \frac{m}{r^2 k} \dots \dots \dots (9).$$

This is the equation giving the resulting concentration in the coloured spot, and if z represents the increase of concentration, so that

$$C_1 = z + C,$$

and one substitutes

$$C_1 = \frac{m}{r^2 \cdot k}$$

and

$$C = \frac{m}{a},$$

the following equation results:

$$\frac{m}{r^2 k} = z + \frac{m}{a},$$

as

$$a = k \cdot R^2,$$

$$z = \frac{m}{r^2 k} - \frac{m}{R^2 k},$$

$$z = \frac{m R^2 - m r^2}{k \cdot R^2 \cdot r^2}.$$

If we substitute $k \cdot R^2 = a$,
 and $\frac{m}{a} = C$,
 we find $z = C \cdot \frac{R^2 - r^2}{r^2} \dots \dots \dots (10)$.

Therefore z is found to be equal to the value of the paper-constant P of Holmgren (3).

Holmgren was of opinion that the relation between the resulting concentration C_1 in the paper and the original concentration C can be expressed by the quotient $\frac{R^2}{r^2}$, so that

$$C_1 = \frac{R^2 C}{r^2} \dots \dots \dots (11).$$

This view seems to be correct, for putting

$$C_1 = \frac{R^2 \cdot C}{r^2} = \frac{m}{r^2 k},$$

we find $R^2 \cdot C \cdot k = m$, and substituting $R^2 k = a$, the definition of $C = \frac{m}{a}$ results.

When Holmgren eliminated $r^2 = \frac{C \cdot R^2}{P + C}$ out of the equation (3) and substituted this value for r^2 in the equation (11), he got

$$C_1 = P + C \dots \dots \dots (12).$$

Therefore Holmgren's paper-constant corresponds with z in equation (10) representing the increase of concentration by the adsorption, P therefore not being a constant but a function of the concentration in question. The following table shows the values for C_1 calculated by the equation (9), P calculated by the equation (2) and C_1 calculated by formula (12).

TABLE X.

Paper No. 123. Congo-red. One drop ($a=0.116$ gr.). $k=0.20923$.

$C = \% \text{ HCl}$	$C_1 = \frac{m}{r^2 \cdot k}; \%$	$P = C \frac{R^2 - r^2}{r^2}$	$C_1 = P + C$	$\frac{P=0.441}{C_1=0.441+C}$
2.0	2.32	0.305	2.305	2.441
1.0	1.44	0.432	1.432	1.44
0.75	1.23	0.475	1.225	1.19
0.5	0.994	0.505	1.005	0.94
0.4	0.894	0.488	0.888	0.841
0.3	0.777	0.472	0.772	0.741
0.2	0.724	0.520	0.720	0.641
0.1	0.554	0.451	0.551	0.541
0.05	0.373	0.321	0.371	0.491

Mean of $P=0.441$.

TABLE X (cont.)

Paper No. 117. Congo-red. One drop ($a=0.116$ gr.). $k=0.1651$.

$C = \% \text{ HCl}$	$C_1 = \frac{m}{r^2 \cdot k} (\%)$	$P = C \frac{R^2 - r^2}{r^2}$	$C_1 = P + C$	$P = 0.285$ $C_1 = 0.285 + C$
1.0	1.19	0.194	1.194	1.285
0.75	1.05	0.299	1.049	1.035
0.5	0.825	0.325	0.825	0.785
0.4	0.668	0.286	0.686	0.685
0.3	0.593	0.292	0.592	0.585
0.2	0.524	0.323	0.523	0.485
0.1	0.377	0.277	0.377	0.385

We see that the values given by $C_1 = \frac{m}{r^2 k}$ and $C = P + C$ are almost identical as the theory demands. But if P is supposed to be constant according to Holmgren, and if the average value is taken for P , we find that the values no longer agree so closely. This difference is better demonstrated by the graphic method in constructing the C - C_1 -curve (Fig. 3).

Fig. 3.

It is evident that $C_1 = P + C$ represents a straight line, which cuts the C_1 -axis at a distance P from the origin and the inclination of which must be 45° .

$C_1 = \frac{m}{r^2 k}$ represents a parabola, by means of which it is possible to demonstrate the fact that for $C = 0$, C_1 must also be 0, a fact which is not expressible by $C_1 = P + C$, P supposed to be constant.

In reality, as P varies with the concentration, the equation $C_1 = P + C$ represents a system of parallel straight lines and the points indicating the relation between C and C_1 follow the course of a parabola cutting this system.

Nevertheless, the disagreement between Holmgren's supposition and the observed values is so slight, that for concentrations not under 0.1 % his method is for practical purposes very useful on account of its extraordinary facility. To demonstrate the very close agreement of the calculation by Holmgren's formula (2) with the reality I give the following table:

TABLE XI.

Paper 123. $a = 0.116$ gr.

$C = \% \text{ HCl}$	$P = 0.441 \text{ (const.)}$ $C = P \frac{r^2}{R^2 - r^2}$	$m = \sqrt[0.273]{\frac{r}{18.88}}$ $\frac{m}{a} = \%$
2.0	2.87	1.4
1.0	1.02	0.989
0.75	0.69	0.77
0.5	0.43	0.53
0.4	0.36	0.44
0.3	0.28	0.33
0.2	0.16	0.18
0.1	0.097	0.084
0.05	0.068	0.048

With regard to a possible combination of the dye and the acid in the paper, the amount of Congo-red or methyl-orange can be approximately calculated. Bayliss [1906] has shown in regard to Congo-red, that the staining of paper is an adsorption process. The temperature-coefficient of the reaction-velocity is so low, that at room temperature at least 24 hours are required for the attainment of equilibrium. I used a clear looking alcoholic solution of Congo-red (0.04 %) and of methyl-orange (0.1 %) always at room-temperature, and dipped the piece of paper into these solutions only for a few seconds, then allowing the alcohol to drain off and drying the paper at 37°. It can therefore be presumed that the amount of dye adsorbed is very small, and if it be assumed that in so short a time only that amount of Congo-red (or methyl-orange) can be adsorbed which was present in the solution filling the interstices of the paper-fibres, the possible error is certainly very small.

Of an 0.04 % alcoholic Congo-red solution each cmm. contains $4 \cdot 10^{-7}$ g. dye,

or in case of 0.1 % methyl-orange $0.1 \cdot 10^{-7}$ g. dye. As already shown, the volume of the interstices, which belongs to a surface of πr^2 , has been found to be $r^2 \cdot k$. According to Table I r was found = 10 mm. in case of an 0.1 % HCl, which gives $r^2 \cdot k = 20.9$ or 21 cmm. Therefore the amount of dye adsorbed in these 21 cmm. is in case of Congo-red $84 \cdot 10^{-7}$, and in case of methyl-orange $2.1 \cdot 10^{-7}$. The same consideration gives $2.1 \cdot 10^{-7}$ as the amount of an 0.1 % HCl in the same volume of interstices.

These figures are mentioned although I was not able to prove that any chemical action resulting in a perceptible decrease in the amount of free acid took place between dye and acid. No difference in the measurement of the radii of the acid-circles could be observed on varying the concentration of the indicator-solution. Holmgren, who compared the effect of 1.0 and 0.1 % solutions of Congo-red in water on the extent of the surface produced by allowing a drop of acid to fall on paper under similar conditions, thought it also very improbable that the amount of dye by itself plays any important part.

But if the effect of adsorption in unstained paper is compared with that obtained in stained paper, a difference can be observed.

Experimenting under the conditions described in the introduction, one observes in unstained paper that the extent of the water-zone exceeds by 2.5 mm. that found in paper stained by the alcoholic indicator-solutions. This difference in the extent of the water-zone is constant, when the concentration of the acid employed varies, a fact which agrees with the circumstance that R is independent of the concentration.

The extent (r) of the acid-spot is also less in stained paper than in unstained, but according to observation this difference increases the more the acid has been diluted, which favours the idea that a chemical action occurs between acid and indicator.

The weight of about 500 gr., which I used to prevent the paper from wrinkling, influences the extent of the water-zone, but the enlargement caused by the pressure is very insignificant and does not exceed 0.1 mm.

In studying the influence of pure alcohol on the paper regarding the adsorption of hydrochloric acid and the capillary extension of water, experiments showed that pure alcohol has an inhibiting action on water as well as on diluted acid.

I may suggest that the fibres of the paper when treated by alcohol, whether pure or combined with dye, are inhibited or prevented from swelling by water, and thus the interstices become larger, which would explain the observation that the radii become smaller.

To apply these considerations to the method which involves the measurement of the capillary height in strips of paper the different volume of liquid must be taken into account. Skraup and his co-workers [1910] were able to show that the amount of water raised in strips of filter-paper is different in different parts of the strip, decreasing in a hyperbolic manner [p. 887]. Whether a similar decrease of the amount of water occurs in the case of a drop producing a circle on the filter-paper is not proved, and I think it very improbable, believing that this phenomenon depends upon gravitation and therefore upon the inclination of the strip, the influence of which is shown by Goppelsroeder [1909] in regard to the capillary height.

I found also in strips of paper that the fact whether they are untreated, stained by alcoholic Congo-red solutions or only treated by pure alcohol, must be taken in account. Thus under the same experimental conditions distilled water rises quicker in the unstained paper and the contrary takes place in case of a dilute hydrochloric acid.

The following table contains measurements of capillary heights in mm., the time having been constant for each experiment, but I could not find any satisfactory explanation of the phenomenon.

		Paper 123 untreated	Treated by	
			Pure alcohol	Congo-red
Diluted HCl	Water	59	71	71
	Acid	50	59	59
Distilled water	{	85	105	77
		66	78	62
		76	89	69

Holmgren [1908] found that the relation between the capillary heights of the acid and the water increases according to the concentration, and that this relation is constant for the same concentration; Skraup and his co-workers [1910] found for all acids (with a few exceptions) that the stronger the acid the higher is the degree of adsorption and *vice versa*.

I hope later to be able to show how the mathematical considerations described in this paper can be applied also to Goppelsroeder's and Skraup's experimental data obtained by the measurement of the capillary height. But I am conscious of the fact that these formulae are still far from being able to describe all the possibilities in such a complex phenomenon as the adsorption of acids by paper.

CONCLUSIONS.

1. Diluted acids produce a ring system when dropped on blotting-paper, the acid remaining behind the water.
2. The radius r of the coloured circle produced by the acid in the paper is connected with the concentration C by an exponential equation of the form $r = \beta \cdot C^n$.
3. The radius R of the water-zone is independent of the concentration and can be determined by the equation $R = \sqrt{\frac{a}{k}}$, a being the volume of the acid drop in question and k being a constant which depends upon the quality of the [stained] paper.
4. The adsorption causes an increase of concentration. The final concentration is found to be a parabolic function of r .
5. The increment of concentration varies with the initial concentration.
6. Holmgren's calculation, which assumes that the increment of concentration is a constant dependent only upon the quality of the paper, is theoretically incorrect, but it has been shown that it may be useful for practical purposes.

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