method. Somewhere in the region of concentration below 0.0005 M the results should show a curvature, and the slopes of experimental graphs should approach the limiting slopes. Although the present results show no tendency to approach the limiting law, we think that this is simply due to the fact that reliable experiments cannot be obtained from the cells in question at such extreme dilutions.

In view of this well established theoretical requirement there is no doubt that the values of E_0 obtained by the second method of extrapolation are the better.

The writer takes this opportunity to express his appreciation to Professor Herbert S. Harned for his advice and help during the progress of this work.

Summary

1. A study of the lead dioxide–lead sulfate–platinum electrode has been made. Crystalline lead dioxide prepared by electrolysis was found to give most consistent results. The reproducibility was within ±0.1 mv.

2. Measurements of the cell

$$H_2 \mid H_2SO_4(m) \mid PbSO_4 \mid PbO_2 \mid Pt^+$$

have been made over a concentration range of 0.0005 to 7.0 M and at temperatures from 0 to 60° at 5° intervals.

3. Values of the molal electrode potentials of the lead sulfate–lead dioxide–platinum electrode have been computed from 0 to 60°. Results by two methods of extrapolation have been discussed.

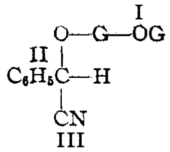
NEW HAVEN, CONN. RECEIVED AUGUST 14, 1934

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF CAMBRIDGE UNIVERSITY]

Activities and the Hydrolysis of Sucrose with Concentrated Acids

BY VERNON K. KRIEBLE

The influence of the common acids as catalysts has been investigated in many reactions but for the most part only in low concentrations. That the velocity constants for these acids, when used as catalysts, go up faster than their conductivities is well known, but it is not generally recognized that this divergence, for some reactions at least, becomes very great beyond a normal solution. Nor is it common knowledge that there is a large difference in velocities between equivalent concentrations of the common acids in moderately high concentration. It was not until Lewis[1] introduced the concept of the activity of ions and molecules, a property which can be measured over a wide limit of concentrations, that there was any reasonable basis for the explanation of these results.

J. W. Walker and the author[2] showed in 1908 the great difference in hydrolytic products produced where amygdalin was hydrolyzed with concentrated solutions of hydrochloric, sulfuric, oxalic and trichloroacetic acids. The amygdalin molecule 

$$\overset{\mathrm{II}}{\mathrm{C_6H_5}}\overset{\overset{\mathrm{I}}{\mathrm{O{-}G{-}OG}}}{\underset{\underset{\mathrm{III}}{\mathrm{CN}}}{\mathrm{C}}}\mathrm{{-}H}$$

has three points where water may be added. Concentrated hydrochloric acid attacks III readily, I moderately, and II least of all; concentrated sulfuric acid attacks II readily and III very little; concentrated oxalic acid attacks I most readily, then II and III very little, while concentrated trichloroacetic acid does not appear to have an appreciable effect on any of them. It was also pointed out that when the concentration of hydrochloric acid was increased in the ratio of 10 to 13 the velocity increased ten-fold. We believe that these are the first experiments on record which showed conclusively that hydrolysis could not be explained as a function of the hydrogen ion alone.

In 1927[3] we showed that there was a wide difference in velocity constants for hydrogen cyanide hydrolysis with equivalent concentration of hydrochloric and sulfuric acids, the former being much more active. It was pointed out that the velocity constants with hydrochloric acid increased at approximately the same rate as the square of the activity of the hydrogen ion or what Lewis and Randall call the activity of the undissociated molecule. This work was extended by Krieble and Peiker,[4] who pointed out that there was a wide difference between hydrogen chloride and hydrogen bromide and that the addition of

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(1) Lewis, *Z. physik. Chem.*, **61**, 129 (1907).

(2) Walker and Krieble, *J. Chem. Soc.*, **95**, 1369 (1909).

(3) Krieble and McNally, THIS JOURNAL, **51**, 3368 (1929).

(4) Krieble and Peiker, *ibid.*, **55**, 2326 (1933).

chlorides to hydrochloric acid increases the rate nearly five times in some cases.

All these experiments, however, have been carried out on substances having the nitrile radical, the hydrolysis of which converts it into the carboxyl radical. It seemed worth while to extend the investigation of concentrated acids on hydrolysis to other groups, particularly since the recent results of Taylor[5] on the hydrolysis of acetamide with strong acids differ markedly from those obtained with the same acid concentrations on hydrogen cyanide. Sucrose was chosen because the hydrolysis of this substance has generally been associated with the hydrogen ion. Early investigators believed that the velocity constants varied as the hydrogen ion concentration but later workers find a better correlation with the activity of the hydrogen ion[6,7] although only in a few cases has this reaction been studied with acids more concentrated than normal and the velocities compared with the hydrogen ion activity. Duboux and Mermond[7] studied hydrochloric acid and nitric acid, but did not carry their investigation beyond 3.6 normal. Hantzsch and Weissberger[8] studied a series of acids up to 4 normal but did not correlate their velocities with activity measurements. In the present investigation the concentration of hydrochloric acid has been extended to 8 normal and sulfuric acid to 10 normal and the velocity coefficients compared with the activities of the hydrogen ion and the undissociated molecule. From these results it seems evident that the rates of hydrolysis do not follow either the activity of the hydrogen ion nor the activity of the molecule.

Experimental

Apparatus.—A Schmidt and Haensch triple field polarimeter sensitive to 0.01° was used to follow the velocity of the reaction. The tube was 200 mm. in length, made of quartz, jacketed, and water from the thermostat pumped around it at a rapid rate. The thermostat was kept at 20 ± 0.03°.

Materials. Sucrose.—A high grade sugar was used. It had a specific rotation of +78.48° at 20° for the sodium line in a 0.146 molal solution. It was not purified further.

Acids.—The hydrochloric and sulfuric acids were the C. P. grades supplied by Harrington Bros. The hydrobromic acid was the A. R. grade made by The British Drug Houses. Part of the hydrobromic acid was redistilled from red phosphorus and the velocity constant for a 4 normal solution redetermined. It proved to be the same as that found with the original acid.

Starting the Reaction.—2.5 grams of sucrose was dissolved in 3 cc. of water in a wide-mouthed covered flask. The requisite amount of acid was measured from a calibrated buret into another wide-mouthed flask and diluted with water to 45.5 cc. so the total volume to which the 2.5 g. of sucrose was added was 48.5 cc. and the molalities refer to this volume. Both flasks were covered, brought to 20° and the acid poured quickly into the sugar solution when the experiment was to be started. The solution was poured back and forth eight to ten times and then into the polarimeter tube. With a little practice this could be done in twenty-five seconds and the first reading was frequently made forty-five seconds after the acid touched the sugar solution. With the more concentrated acids, there was a slight temperature change observed when the solutions were mixed. When a preliminary experiment showed this to be the case the acid solution was brought to such a temperature that, when mixed with the sucrose

TABLE I

C = 1.05 molal HCl
a = 10.40

t, min.	$a - x$	$k \times 10^2$
122	5.31	0.2395
140	4.81	.2395
215	3.15	.2408
235	2.83	.2405
270	2.34	.2400
288	2.10	.2400

C = 3.28 molal HCl
a = 10.60

15.5	5.35	0.1915
18.5	4.69	.1916
21	4.21	.1910
25	3.52	.1915
29	2.95	.1918
32	2.59	.1912
35	2.27	.1910

C = 8.48 molal HCl
a = 5.70

0.50	3.70	0.376
.64	3.30	.371
.77	2.95	.372
.87	2.66	.381
.98	2.30	.406
1.12	2.05	.396
1.23	1.75	.417
1.35	1.68	.393
1.50	1.51	.385
1.60	1.35	.391
1.83	1.08	.394
2.03	0.90	.394
2.29	.75	.385
2.54	.63	.377
2.88	.46	.381
3.05	.40	.379
3.22	.32	.383

C = 5.0 N HBr
a = 9.59

t, min.	$a - x$	k
2.15	4.93	0.155
2.70	4.12	.152
3.08	3.52	.155
3.62	2.94	.154
4.43	2.20	.154
5.30	1.63	.153
6.33	1.09	.156
7.53	0.71	.156
8.97	.43	.157
10.75	.23	.156

C = 8.48 molal HCl
a = 5.70

0.17	4.85	0.414
.30	4.30	.408
.48	3.65	.404
.61	3.20	.411
.73	2.90	.402
.87	2.60	.392
.98	2.30	.402
1.13	2.10	.384
1.37	1.70	.384
1.63	1.35	.384
1.80	1.15	.386
1.97	0.92	.402
2.17	.80	.392
2.30	.70	.396
2.48	.64	.384
2.63	.50	.402
2.77	.44	.404
2.93	.42	.398
3.11	.32	.402
3.41	.25	.397
3.60	.22	.393

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(5) Taylor, *J. Chem. Soc.*, 2741 (1930).

(6) For references up to 1927 see Rice, A. C. S. Monograph, "The Mechanism of Homogeneous Organic Reactions," 1928.

(7) Duboux and Mermond, *Helv. Chim. Acta*, **11**, 583 (1928); Conant and Hall, THIS JOURNAL, **49**, 3062 (1927); Bowe, *J. Phys. Chem.*, **31**, 291 (1927).

(8) Hantzsch and Weissberger, *Z. physik. Chem.*, **128**, 258 (1927).

solution, the temperature of the mixture was 20 ± 0.3°. That this method gives accurate and reproducible results even for very fast reactions is illustrated in Table I.

Initial Rotation.—Pennycuick[9] has pointed out the importance of determining the initial rotation experimentally if the velocity constants during the early stage of the reaction are to have any value. This, unfortunately, is not possible with concentrated acids. The first reading was therefore taken as the initial value for the concentrated acid solutions. For those below 4 molal we extrapolated to $t = 0$ according to the method of Rosanoff, Clarke and Sibley.[10] In determining the velocity constant for a given acid concentration, the values obtained during the 50–80% range of hydrolysis were averaged as suggested by Rice, Fryling and Wesolowski.[11] If this method is applied to the table given by Pennycuick[12] where he uses four different initial values for the same reaction, the velocity constant varies only 1 in 600, irrespective of how the initial value is chosen.

Final Rotation.—This was determined by experiment. The reaction was considered complete when a time interval had elapsed four to five times that required to reach 95% hydrolysis. For solutions up to 4 molal these final rotations remained constant for days. Stronger solutions, particularly 8 and 9 molal hydrochloric acid solutions, were pink the next day and showed a decrease in rotation. That this slow decomposition does not interfere in any way with the determination of the rate of reaction is evident from Table I, where the velocity for an 8.48 molal hydrochloric acid solution remains constant to 95% hydrolysis. Had the final rotation been out even a few hundredths of a degree, the velocity constants near the end would have varied enormously.

Calculation of Velocity Constants.—The usual formula for a monomolecular reaction was used: $k = 1/t \log_{10} a/(a-x)$, where a represents total change of rotation and x the difference between the initial rotation and the rotation at time t.

Discussion

Hydrochloric Acid.—The results of the experiments with this acid are given in Table II. While the acid concentration increased nearly 10 times in terms of molality, the velocity constant increased 363 times. There is no relationship between concentration of acid and rate of hydrolysis.

In the case of hydrogen cyanide it was found as previously stated that there was a fairly good correlation between the square of the activity of the H ion a^2 and the rate of hydrolysis. At 30° for example $k \times 10^5$ divided by a^2 for the molalities of 2.03, 4.26, and 6.67 gave 2.16, 2.97 and 2.44, respectively. The conclusion was drawn, therefore, that the hydrolysis of hydrogen cyanide was caused by the hydrogen chloride molecule. It might equally well be explained by assuming that it was a combination of the H ion and the Cl ion which, $HCN + H^+ + Cl^- + 2H_2O = HCOONH_4$, catalyzed the reaction. At any rate the reaction is similar to the conversion of acetylchloroaminobenzene to *p*-chloroacetanilide studied by Rivett, Harned and Seltz, and Åkerlöf[13] who found that $K = k/a_{H}a_{Cl}$ where k is the observed unimolecular velocity constant and K is also a constant and is independent of the acid strength. They, however, did not go above one molal acid concentration. Column 4, Table II, shows that no such relationship holds for the hydrolysis of sucrose.[14]

TABLE II[14]

Molality of HCl	Velocity constant k	$\frac{k \times 10^3}{a_\pm}$	$\frac{k \times 10^3}{(a_\pm)^2}$
1.05	0.0024	2.78	3.25
2.14	.00779	3.36	1.46
3.28	.0191	3.95	0.81
4.44	.0409	4.33	.46
5.72	.0860	4.72	.26
7.08	.179	5.25	.15
8.48	.392	6.4	.10
9.96	.872	8.28	.08

Pennycuick[9] concluded that for a definite concentration of water and sugar, the velocity constant varied as the hydrogen-ion activity for hydrochloric acid concentrations to 1 normal. Duboux and Mermond[7] concluded that, up to 3.6 normal, the velocity followed as a first approximation the activity of the hydrogen ion. Our results agree with these conclusions. Above 4 molal acid concentration, however, the velocity of hydrolysis goes up faster than the activity of the H ion, as is evident from column 3, Table II. This suggests a second catalyst. It is quite possible that a combination of the H ion and the Cl ion or the undissociated molecule is this second catalyst. Then

$$K = k_1 a_\pm + k_2 (a_\pm)^2 \qquad (1)$$

where K is the velocity constant and $a_\pm$ the activity of the H ion and $(a_\pm)^2$ the activity of the hydrogen and chlorine ions or the activity of the undissociated molecule.

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[9] Pennycuick, *J. Chem. Soc.*, **125**, 2049 (1924); THIS JOURNAL, **48**, 6 (1926).

[10] Rosanoff, Clarke and Sibley, *ibid.* **33**, 1911 (1911).

[11] Rice, Fryling and Wesolowski, *ibid.*, **46**, 2045 (1924).

[12] Ref. 9, *ibid.*, Table IV, p. 12.

[13] Taylor, "Treatise on Physical Chemistry," 1924, D. Van Nostrand Co., New York, p. 780.

[14] Unless stated otherwise all numerical values for activities refer to interpolated values taken from Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923. Their notation is used throughout. The hydrogen-ion activity is taken as the mean ion activity $a_\pm$.

To test this hypothesis the following two simultaneous equations were formed from the velocities for 3.28 and 9.96 molal hydrochloric acid solutions and the activities for the hydrogen ion and the hydrochloric acid molecule for these acid concentrations.

$$0.0191 = 4.82k_1 + 23.38k_2 \quad (2)$$

$$0.872 = 105.24k_1 + 11{,}111k_2 \quad (3)$$

The solution of these equations gives a value of 0.00375 for k_1 and 0.0000403 for k_2. If one substitutes in equation 1 these values for k_1 and k_2 and the activities for the hydrogen ion and the hydrochloric acid molecule for any acid concentration, it should be possible to calculate the velocity constant for that acid concentration. This has been done for molalities 1 to 10 and the results given in column 6, Table III. With the exception of molalities 1 and 2 the agreement is good—especially if it is taken into consideration that the activities are interpolated from values measured at 25° and without any sugar present. If our hypothesis is correct that the hydrolysis is catalyzed partly by the hydrogen ion and partly by the undissociated molecule, then columns 4 and 5 of Table III give the relative part of the velocity catalyzed by each at the various concentrations.

TABLE III

Molality	$a_{\pm}$	$(a_{\pm})^2$	$k_1 \times a_{\pm}$	$k_2 \times (a_{\pm})^2$	k calcd.	k obsd.
1.05	0.863	0.7465	0.00324	0.00003	0.00327	0.0024
2.14	2.318	5.318	.0087	.00022	.0089	.00779
3.28	4.826	23.38	.018	.0010	.0191	.0191
4.44	9.440	89.12	.035	.0036	.0393	.0409
5.72	18.20	331.10	.068	.0130	.083	.086
7.08	34.04	1,149.00	.128	.0469	.177	.179
8.48	61.23	3,750.00	.23	.162	.392	.392
9.96	105.24	11,111.00	.395	.453	.872	.872

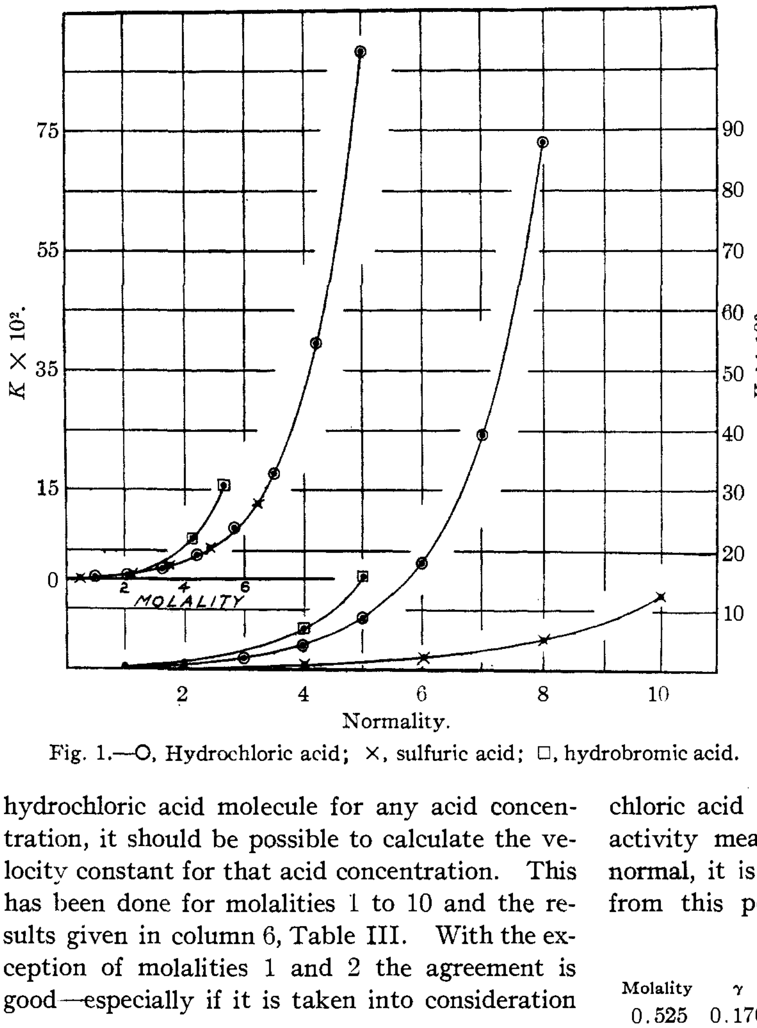

Fig. 1.—O, Hydrochloric acid; ×, sulfuric acid; □, hydrobromic acid.

Sulfuric Acid.—Figure 1 gives a comparison of hydrochloric acid and sulfuric acid on the basis of normality and molality. On the basis of equivalents hydrochloric is by far the best catalyst but on a molality basis sulfuric acid is practically identical with hydrochloric. It seemed worth while to compare again the velocity constants with activities. Lewis and Randall give the activity coefficients γ for sulfuric acid for various molalities. By definition the activity coefficient, γ, times the molality, m, equals the mean ion activity $a_{\pm}$. As sulfuric acid ionizes principally into H^+ and HSO_4^- ions in moderately concentrated solutions, the activity of the molecule a_2 equals a_+a_- or $(a_{\pm})^2$. That the velocity of hydrolysis again goes up faster than $a_{\pm}$, the mean ion activity, and not as fast as the square of ion activity is evident from columns 6 and 7, Table IV.

Hydrobromic Acid.—Table V gives the velocity constants for hydrobromic acid from 1 to 5 normal. A comparison with hydrochloric acid is made in Fig. 1. As there are no activity measurements for this acid above 1.5 normal, it is impossible to discuss these results from this point of view. It is interesting to compare our results with those of Hantzsch and Weissberger, who carried out their experiments at 25° as it gives the temperature coefficient 25/20.

TABLE IV

Molality	γ	$\gamma \times m$ $a_{\pm}$	$(a_{\pm})^2$ a_2	K obsd.	$K/a_{\pm}$	K/a_2
0.525	0.170	0.089	0.0079	0.00106	0.012	1.33
1.070	.149	.160	.0255	.00272	.017	0.106
2.230	.150	.335	.1120	.00870	.026	.077
3.510	.184	.812	.6600	.02220	.027	.034
4.910	.239	1.180	1.3800	.05110	.043	.037
6.520	.338	2.210	4.8600	.12700	.057	.026

The table also gives the temperature coefficients for hydrochloric and sulfuric acids for this range using the values of Hantzsch and Weissberger for 25°.

TABLE V

Normality	HBr velocity constant *k*	HBr 25/20	HCl 25/20	H_2SO_4 25/20
1	0.00278	2.46	2.39	2.5
2	.00995	2.38	2.3	2.53
4	.06680	2.46	2.4	2.61
5	.1540			

The author wishes to express his thanks and appreciation to Professor T. M. Lowry for putting at his disposal the facilities of the Cambridge laboratory to carry out this research.

Summary

1. Velocity constants have been determined for sucrose hydrolysis in a 0.146 molal solution using hydrochloric acid from 1 to 9.96 molal, sulfuric acid from 0.525 to 6.52 molal and hydrobromic acid from 1 to 5 normal as catalysts.
2. The velocity constants are not directly proportional to either the concentration of the acid or the hydrogen-ion activity for hydrochloric or sulfuric acid.
3. The velocity constants can be calculated fairly accurately from the activities and therefore from e. m. f. measurements from a 3 molal to a 10 molal hydrochloric acid solution.
4. The hypothesis is put forward that sucrose hydrolysis with hydrochloric acid is catalyzed partly by the hydrogen ion and partly by the molecule or both ions. In a 1 molal solution, 99% is hydrolyzed by the hydrogen ion while in a 10 molal solution it hydrolyzes only 45%.
5. No simple relationship was observed between activities and velocity constants for sulfuric acid.
6. The ratios between the velocity constants for 20 and 25° have been calculated for hydrochloric, sulfuric and hydrobromic acids using the velocity constants obtained by Hantzsch and Weissberger for 25°.

HARTFORD, CONN. RECEIVED AUGUST 21, 1934

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF TRINITY COLLEGE]

The Electromotive Force Measurements of Hydrochloric Acid Solutions with and without Sucrose and their Relation to the Rate of Sucrose Hydrolysis[1]

BY VERNON K. KRIEBLE AND FRED M. REINHART

In the previous paper evidence was submitted which seemed to indicate that the rate of hydrolysis of sucrose could be correlated with the electromotive force of the solution. The electromotive force measurements used, however, were those for pure hydrochloric acid solutions made at 25° instead of acid solutions containing sugar at 20°, at which temperature the hydrolysis was measured. It seemed worth while, therefore, to measure the electromotive force of such solutions to make certain that there was a real correlation between these two factors.

Experimental

Part I. Electromotive Force Measurements

Apparatus.—The null method was used for the electromotive force measurements, using a Leeds and Northrup Type K potentiometer, a type 2500-a galvanometer, an Eppley standard cell and a calomel and a bubbling hydrogen electrode. The apparatus was suspended in a thermostatic bath maintained at 20 ± 0.02°.

Experimental Procedure

Sucrose.—Bureau of Standards, Standard Sample 17 of sucrose was used for these measurements because it was found that the sucrose purified in this Laboratory and other grades were not of sufficient purity to give reproducible results as shown in the table; *T* is time in hours and *E* is volts.

TABLE I

Purified sucrose		Commercial sucrose		Crystal sucrose		Sample 17 sucrose	
T	*E*	*T*	*E*	*T*	*E*	*T*	*E*
2.00	0.22810	2.00	0.22855	2.00	0.22760	0.10	0.22675
2.50	.22183	3.00	.22904	3.00	.22842	0.50	.22843
3.00	.22822	4.00	.22942	4.00	.22865	1.00	.22833
3.50	.22825	5.00	.22940	5.00	.22884	1.25	.22829
4.00	.22837	6.00	.22955	6.00	.22902	1.50	.22824
5.00	.22862	7.00	.22966	7.00	.22917	1.75	.22821
6.00	.22925	8.00	.22974	8.00	.22927	2.00	.22822
6.50	.22956	9.00	.22980	9.00	.22931	2.50	.22825
9.50	.22984	10.00	.22984	10.00	.22942		
15.00	.22996	15.00	.22995	15.00	.22954		
24.25	.22986	25.50	.22994	25.50	.22956		

Mercury.—This was triply distilled and further purified by the electrolytic method.

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[1] From a master's thesis submitted by F. M. Reinhart in partial fulfilment of the requirements for a Master's degree at Trinity College, 1933.