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CONTRASTING EFFECTS OF CHLORIDES AND SULFATES ON THE HYDROGEN ION CONCENTRATION OF ACID SOLUTIONS.

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In the process of chrome tanning the practical tanner has discovered that by addition of neutral salts it is possible to use more basic chrome liquors. The added salt prevents the precipitation of hydrous chromic oxide. Wilson and Kern[1] believe that this phenomenon is due to increase in the hydrogen ion concentration caused by removal of water from the solvent to hydrate ions of the added salts.

Since Wilson and Kern did not actually measure the hydrogen ion concentration of these solutions, the authors of this paper took up the problem with the result that a striking contrast in the effect of chlorides, and sulfates and magnesium salts on solutions of hydrochloric and sulfuric acids has been noted.

In our first experiment the effect of sodium chloride, ammonium chloride, sodium sulfate, ammonium sulfate and magnesium sulfate upon the hydrogen ion concentration of a stock chrome liquor,[2] diluted to contain 13.86 g. of chromic oxide per liter, was determined. These figures are given in Table I and Fig. 1.

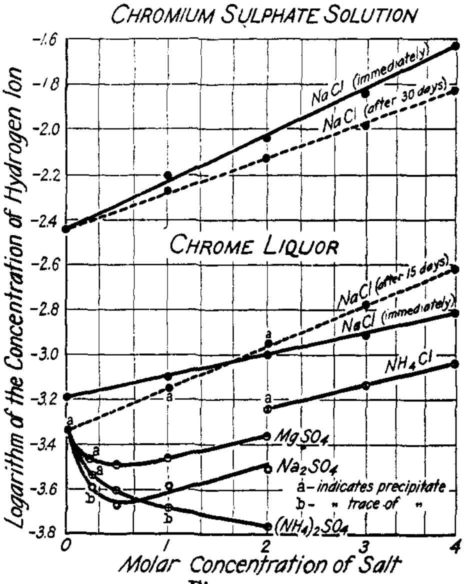

Fig. 1.

It will be noted that equilibrium in hydrogen ion concentration is not reached immediately after dilution of a concentrated chrome liquor by water or by salt solution. This effect is shown in Table II and Fig. 2. This slow increase in hydrogen ion concentration in solutions of chromic salts has been long known and has been shown to be due to the trans-

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[1] *J. Am. Leather Chem. Assoc.*, **12**, 445 (1917).

[2] This stock chrome liquor analyzed by and furnished to us by Mr. John Arthur Wilson, of Milwaukee, showed: Cr_2O_3, 14.3%; Fe_2O_3, 1.9%; Al_2O_3, 0.2%; SO_3, 23.5%; NaCl, 0.4%; glucose, none; sp. g., 1.628 at 80° F.

TABLE I.

Effect of Neutral Salts upon the Concentration of Hydrogen Ion of Chrome Liquor.

Sodium Chloride.

Concentration of salt. Molar strength.	Log C_{H^+} immediately.	Log C_{H^+} after 15 days.
0	—3.19	—3.33
1	—3.10	—3.14
2	—3.00	—2.95
3	—2.92	—2.78
4	—2.81	—2.62

Ammonium Chloride.

Concentration of salt. Molar strength.	Log C_{H^+} after 30 days.
0	—3.33
2	—3.24
3	—3.14
4	—3.04
5	—2.95

Sodium Sulfate.

Concentration of salt. Molar strength.	Log C_{H^+} after 30 days
0	—3.33
0.25	—3.59
0.5	—3.67
1.0	—3.58
2.0	—3.51

Ammonium Sulfate.

Concentration of salt. Molar strength.	Log C_{H^+} after 30 days.
0	—3.33
0.25	—3.54
0.5	—3.60
1.0	—3.68
2.0	—3.77

Magnesium Sulfate.

Concentration of salt. Molar strength	Log C_{H^+} after 30 days.
0	—3.33
0.25	—3.47
0.5	—3.49
1.0	—3.46
2.0	—3.36

Effect of Sodium Chloride on Chromium Sulfate Solution.

Concentration of salt. Molar strength.	Log C_{H^+} immediately.	Log C_{H^+} after 30 days.
0	—2.43	—2.43
1	—2.22	—2.28
2	—2.04	—2.13
3	—1.84	—1.98
4	—1.63	—1.83

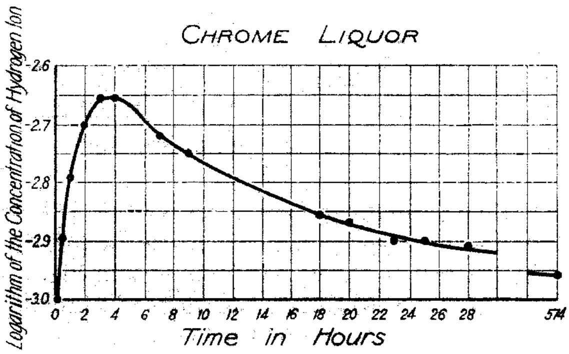

Fig. 2.

formation of the acido chromic salt into a more largely hydrolyzed hexaaquo salt.[1]

The effect noted above is not due entirely to the added salt, as can be observed in Table I and Fig. 1, where the log C_{H^+} of the chrome liquor with no added salt was observed to be —3.19 immediately after dilution and —3.33 fifteen days after dilution.

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[1] Bjerrum, *Z. physik. Chem.*, 89, 336 and 581 (1907); also *Kgl. D. Vid. Selak. Skr.*, [7] 4, 1 (1906).

TABLE II.

Influence of Time upon the Hydrogen Ion Concentration of a Chrome Liquor after Addition of Sodium Chloride and Dilution.

Time, min.	Log $C_{H}+$.	Time, hrs.	Log $C_{H}+$.
10	—3.00	3	—2.66
20	—2.94	4	—2.66
30	—2.89	7	—2.72
40	—2.85	9	—2.75
50	—2.82	18	—2.86
60	—2.79	20	—2.87
70	—2.77	23	—2.90
80	—2.75	25	—2.90
90	—2.73	28	—2.91
100	—2.72	34	—2.92
110	—2.70	46	—2.96
120	—2.70	57	—2.96
130	—2.69	15 days	—2.96
140	—2.69		
150	—2.68		
160	—2.67		
170	—2.66		

The effect of sodium chloride upon a solution of pure chromium sulfate of chromium content equal to that of the chrome liquor is also shown in Table II.

Since a rather complicated system is obtained by the mixture of solutions of chlorides with chromium sulfate it was deemed advisable to compare the effect of chlorides upon pure chromium chloride solutions.

A concentrated solution of the green modification of chromium chloride was made up for use as a stock solution, and this solution was mixed with solutions of the chlorides and then made up to volume to contain chromium chloride equivalent to 13.77 g. of Cr_2O_3 per liter in each case and the added chloride at the concentrations given.

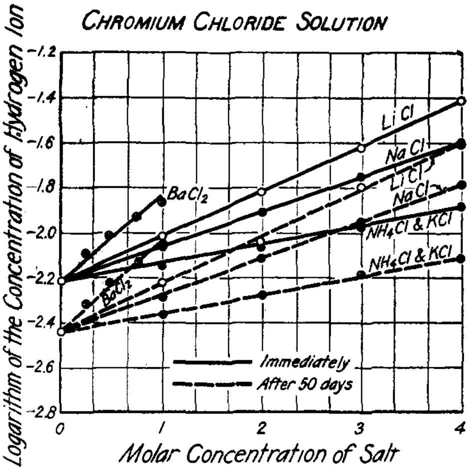

Fig. 3.

The results of these experiments are shown in Table III and Fig. 3.

It is evident that substantially the same phenomena occur here as in the mixture of chlorides and chromium sulfate.

It was then considered expedient to test the effects of chlorides and

TABLE III.

Effect of Chlorides upon the Concentration of Hydrogen Ion of Chromium Chloride Solution.

Concentration of salt. Molar strength.	Log $C_{H}+$ immediately.	Log $C_{H}+$ after 50 days.
	Sodium Chloride.	
0	—2.22	—2.43
1	—2.06	—2.24
2	—1.91	—2.11
3	—1.75	—1.95
4	—1.59	—1.79
	Potassium Chloride.	
0	—2.22	—2.43
1	—2.15	—2.36
2	—2.06	—2.28
3	—1.97	—2.19
4	—1.88	—2.12
	Ammonium Chloride.	
0	—2.22	—2.43
1	—2.14	—2.36
2	—2.07	—2.30
3	—1.97	—2.19
4	—1.88	—2.14
	Lithium Chloride.	
0	—2.22	—2.43
1	—2.01	—2.22
2	—1.82	—2.04
3	—1.62	—1.80
4	—1.41	—1.60
	Barium Chloride.	
0	—2.22	—2.43
0.25	—2.09	—2.32
0.5	—2.02	—2.23
0.75	—1.93	—2.13
1.0	—1.86	—2.05

TABLE IV.

Effect of Salts upon the Concentration of Hydrogen Ion of 0.0005 *N* Sulfuric Acid.

Concentration of salt. Molar strength.	Log $C_{H}+$.	Concentration of salt. Molar strength.	Log $C_{H}+$.
Sodium Chloride.		Ammonium Chloride.	
0	—3.50	0	—3.50
1	—3.29	2	—3.27
2	—3.10	3	—3.14
3	—2.92	4	—3.00
4	—2.71	5	—2.88
Sodium Sulfate.		Ammonium Sulfate.	
0	—3.50	0	—3.50
0.25	—4.37	0.25	—4.00
0.5	—5.10	0.5	—4.00
1.0	—6.05	1.0	—4.00
2.0	—6.92	2.0	—4.00

sulfates on solutions of sulfuric and hydrochloric acids of such concentrations as to give approximately the same hydrogen ion concentrations as the chromium sulfate and chloride. The concentrations were found to be 0.0005 *N* sulfuric acid and 0.004 *N* hydrochloric acid. The results of addition of salts to these acids are shown in Tables IV and V, and Figs. 4 and 5.

The similarity in the contrasting effects of sulfates and chlorides on simple acid solutions of hydrogen ion concentrations equal to those of the chromium sulfate and chloride solutions demonstrates that this phenomenon is not pertinent to solutions of chromium salts alone.

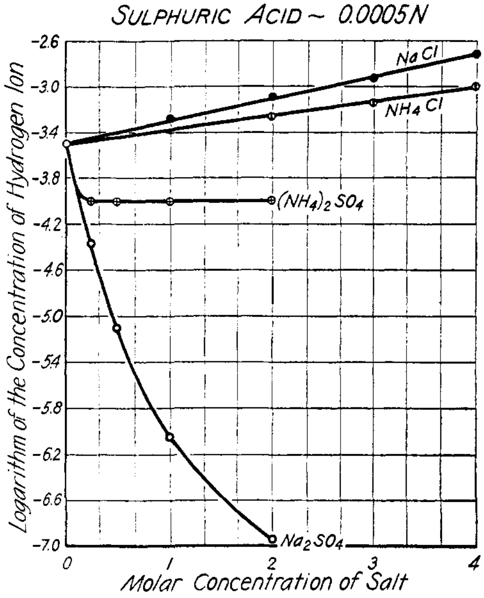

Fig. 4.

Since the effect is general with acid solutions it was considered of importance to make a series of determinations upon acids of 0.1 *N* (equivalent) concentration. Due to the difference in behavior of magnesium sulfate from the other sulfates, magnesium chloride was included with the salts previously tried.

In all cases, a solution of acid was mixed with a solution of a salt and diluted to 100 cc. The concentration of this solution of the mixture was always 0.1 *N* (equivalent) with respect to the acid and that particular concentration of the salt whose effect upon the hydrogen ion concentration was to be studied. The hydrogen ion concentrations were measured two days after the solutions were made up.

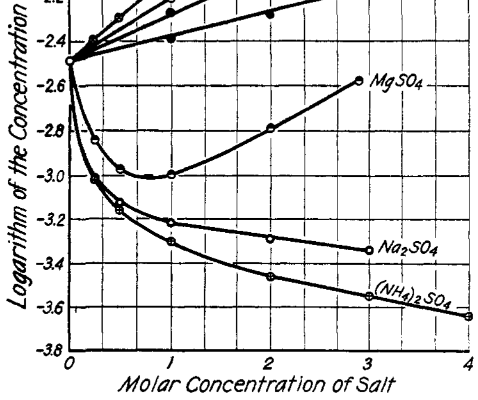

Fig. 5.

TABLE V.

Effect of Chlorides upon the Concentration of Hydrogen Ion of 0.004 *N* Hydrochloric Acid.

Concentration of salt. Molar strength.	Log $C_{H}+$.	Concentration of salt. Molar strength.	Log $C_{H}+$.
Sodium Chloride.		Potassium Chloride.	
0	−2.49	0	−2.49
1	−2.27	1	−2.39
2	−2.10	2	−2.28
3	−1.88	3	−2.17
4	−1.69	4	−2.03
Ammonium Chloride.		Lithium Chloride.	
0	−2.49	0	−2.49
1	−2.37	1	−2.21
2	−2.27	2	−1.95
3	−2.18	3	−1.67
4	−2.03	4	−1.40
Barium Chloride.		Sodium Sulfate.	
0	−2.49	0	−2.49
0.25	−2.40	0.25	−3.01
0.5	−2.30	0.5	−3.13
1.0	−2.10	1.0	−3.22
		2.0	−3.29
		3.0	−3.34
Ammonium Sulfate.		Magnesium Sulfate.	
0	−2.49	0	−2.49
0.25	−3.02	0.25	−2.84
0.5	−3.16	0.5	−2.97
1.0	−3.30	1.0	−2.99
2.0	−3.46	2.0	−2.79
3.0	−3.55	3.0	−2.58
4.0	−3.64		

Tables VI and VII, and Figs. 6 and 7 show the results obtained.

It may be noted here that the relative effect of ammonium sulfate and sodium sulfate on 0.1 *N* sulfuric acid differs from that on 0.0005 *N* sulfuric acid as shown in Fig. 4. In the case of the 0.0005 *N* acid, ammonium sulfate decreases the hydrogen ion concentration at 0.25 molar concentration of the salt and no further decrease is noted for higher concentrations. This is probably due to the slight acid reaction of ammonium sulfate which is noticeable in such dilute acid as 0.0005 *N*, but not in the presence of 0.1 *N* sulfuric acid.

The effect of chlorides in increasing the hydrogen ion concentration of hydrochloric acid solutions is not new. This has previously been shown by Poma,[1] Harned[2] and by Fales and Nelson.[3] Arrhenius[4] found that

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[1] *Z. physik. Chem.*, **88**, 671 (1914).

[2] THIS JOURNAL, **37**, 2460 (1915).

[3] *Ibid.*, **37**, 2769 (1915).

[4] *Z. physik. Chem.*, **31**, 197 (1899).

the hydrogen ion activities of acetic and of hydrochloric acids were increased by neutral salts which he thought was due to the salts increasing the dissociation of the acids, but in the light of recent work on hydration of ions in aqueous solutions, a more plausible explanation is offered,[1] namely, that the volume of solvent appears to decrease.

When the chlorides are arranged in order of their ability to increase the hydrogen ion activity, the following series is obtained: $MgCl_2 > BaCl_2 > LiCl > NaCl > NH_4Cl = KCl$ which, with the exception of magnesium and of barium, is in inverse order to a series of these cations arranged in order of their equivalent conductivities.

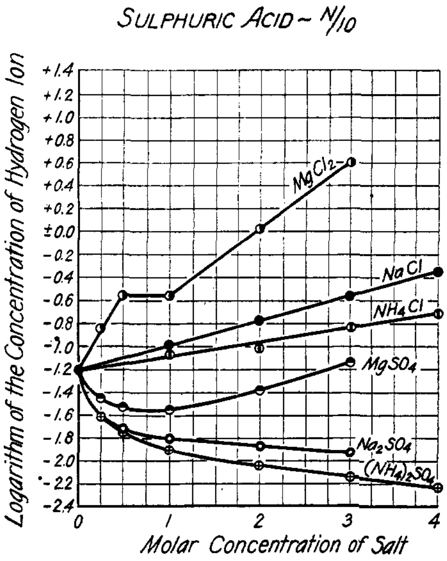

Fig. 6.

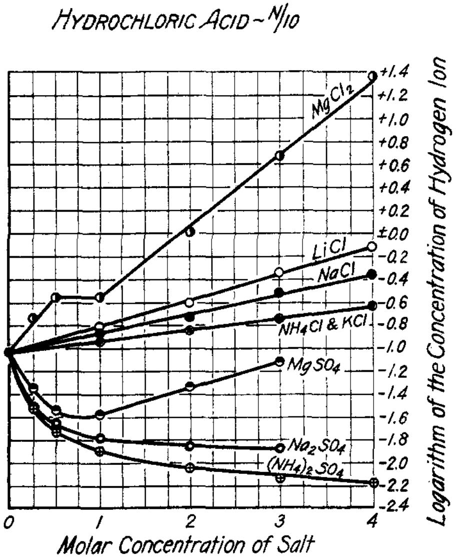

Fig. 7.

In the above series the salts are arranged in order of the increasing hydration (*i. e.*, number of molecules of water combined with the ions at infinite dilution) of their cations, K^+, 9.6; NH_4^+, 10.7; Na^+, 16.9; Li^+, 24.0;[2] Ba^{++}, relatively higher;[3] Mg^{++}, higher than Ba^{++}.[4]

Poma[5] found that chlorides increased the hydrogen ion concentration of hydrochloric acid solutions in the following order: $MgCl_2 > CaCl_2 > LiCl > KCl > RbCl$.

The noteworthy feature of this paper is the contrast shown between the decreasing hydrogen

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[1] Poma, *Loc. cit.* Poma and Patroni, *Z. physik. Chem.*, **87**, 197 (1914); Harned, *Loc. cit.;* Smith, THIS JOURNAL, **37**, 722 (1915).

[2] Smith, *Loc. cit.*

[3] Washburn, *Tech. Quart.*, **21**, 360 (1908).

[4] Jones, *Carnegie Inst. Pub.*, 60 (1907).

[5] *Loc. cit.*

TABLE VI.

Effect of Salts upon the Concentration of Hydrogen Ion of 0.1 *N* Sulfuric Acid.

Concentration of salt. Molar strength.	Log $C_{H}+$.	Concentration of salt. Molar strength.	Log $C_{H}+$.
Sodium Chloride.		Ammonium Chloride.	
0	—1.21	0	—1.21
1	—0.99	1	—1.08
2	—0.78	2	—0.98
3	—0.57	3	—0.84
4	—0.36	4	—0.72
Magnesium Chloride.		Sodium Sulfate.	
0	—1.21	0	—1.21
0.25	—0.84	0.25	—1.60
0.5	—0.56	0.5	—1.72
1.0	—0.56	1.0	—1.80
2.0	+0.03	2.0	—1.88
3.0	+0.60	3	—1.92
Ammonium Sulfate.		Magnesium Sulfate.	
0	—1.21	0	—1.21
0.25	—1.61	0.25	—1.46
0.5	—1.76	0.5	—1.52
1.0	—1.90	1.0	—1.53
2.0	—2.04	2.0	—1.39
3.0	—2.15	3.0	—1.15
4.0	—2.24	...	......

ion effect of sulfates and the increasing effect of chlorides on acid solutions, and the interesting similarity of the distribution of the plots between the sulfuric acid salt systems and the hydrochloric acid salt systems. We are not prepared to offer an explanation for the above but are in agreement with the statement made by Harned[1] that "when more complete thermodynamic data are available, the calculation of equilibria in concentrated solutions will be rendered possible," and that if, as he has indicated "the thermodynamic degrees of dissociation or activities are a simple function of the ionic hydration values, the whole behavior of a concentrated solution of an electrolyte will become explicable."

The peculiar effect of magnesium salts is interesting, especially in that the concentrations for bends in the curves are in each case between 0.5 and 1 molar. We have tried to find an explanation for these peculiarities in Jones' "Hydrates in Aqueous Solutions."[2] Jones states, "Magnesium sulfate, like all the other sulfates studied, gives abnormal results. It appears to form no hydrates in aqueous solution, notwithstanding the fact that it crystallized with seven molecules of water of crystallization. It is almost certain that this substance has considerable hydrating power, but

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[1] THIS JOURNAL, 40, 1481 (1918).

[2] *Carnegie Inst. Pub.* 60 (1907).

this is masked in our results by the large amount of polymerization which the sulfates undergo."

TABLE VII.

Effect of Salts upon the Concentration of Hydrogen Ion of 0.1 *N* Hydrochloric Acid.

Concentration of salt. Molar strength.	Log $C_{H}+$.	Concentration of salt. Molar strength.	Log $C_{H}+$.
Sodium Chloride.		Potassium Chloride.	
0	—1.038	0	—1.038
1	—0.88	1	—0.95
2	—0.72	2	—0.85
3	—0.52	3	—0.75
4	—0.36	4	—0.63
Ammonium Chloride.		Lithium Chloride.	
0	—1.038	0	—1.038
1	—0.94	1	—0.81
2	—0.87	2	—0.60
3	—0.75	3	—0.35
4	—0.65	4	—0.12
Barium Chloride.		Magnesium Chloride.	
0	—1.038	0	—1.038
0.25	—0.96	0.25	—0.73
0.5	—0.88	0.5	—0.55
0.75	—0.80	1.0	—0.55
1.0	—0.71	2.0	+0.005
		3.0	+0.68
		4.0	+1.37
Sodium Sulfate.		Ammonium Sulfate.	
0	—1.038	0	—1.038
0.25	—1.51	0.25	—1.52
0.5	—1.65	0.5	—1.72
1.0	—1.79	1.0	—1.90
2.0	—1.86	2.0	—2.05
3.0	—1.89	3.0	—2.14
		4.0	—2.18
Magnesium Sulfate.			
0	—1.038		
0.25	—1.36		
0.5	—1.45		
1.0	—1.47		
2.0	—1.34		
3.0	—1.12		

The curve of freezing-point depression of magnesium sulfate plotted against concentration shows a depression to about 0.5 molar from which point the depression decreases for higher concentrations. In this respect there is a slight similarity to its decreasing effect on hydrogen ion concentration to 0.5 to 1 molar, beyond which it increases it. Magnesium chloride, however, gave a similar effect on freezing-point depression, although not so pronounced as magnesium sulfate.

We do not believe that the figures for hydrogen ion concentrations in the presence of salts (except in dilute solutions) given in this paper, are the true values. They should be termed apparent concentrations of hydrogen ion as determined by the method in general use at this date.

Apparatus and Method.

For the determination of the hydrogen ion concentration, a Wolff 15,000 ohm bridge with a galvanometer to determine the null point was used. As hydrogen electrode, a No. 16 Brown and Sharpe gage platinum wire (platinized) fused in a glass tube inserted in the Clark[1] cell was used. The calomel element contained 3.5 molar potassium chloride solution saturated with calomel and was the same design as that described by Fales and Vosburgh.[2] The e. m. f. was determined by means of a Weston cell that had been checked by the Bureau of Standards. The hydrogen contained in a tank under pressure, was carefully washed through saturated mercuric chloride solution, alkaline permanganate, alkaline pyrogallol and a tower of cotton fibers. The measurements were made at room temperatures which varied between 22° and 26°, the proper corrections being made. No correction for barometric pressure was made since this correction is so small.[3] No attempt was made to calculate and corrrect for the solution contact potential because we know of no satisfactory method of doing so, especially where solutions containing divalent ions are concerned. It is emphasized, however, that the differences in effects reported in this paper cannot be attributed to solution contact potential. This point was demonstrated by Harned, and Fales and Vosburgh[4] proved that there is no contact potential at 25° between a saturated solution of potassium chloride (4.1 *M*) and hydrochloric acid solutions ranging in concentrations between 0.1 molar and 1.0 molar.

The salt bridge between the hydrogen and calomel elements used in our measurements was a saturated solution of potassium chloride.

We are greatly indebted to the Messrs. A. F. Gallun and Sons Company, of Milwaukee, for grants in aid of this investigation, and to the editor of THIS JOURNAL for his helpful criticism of the manuscript.

NEW YORK, N. Y.

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[1] Clark, *J. Biol. Chem.*, **23**, 475 (1915).

[2] THIS JOURNAL, 40, 129 (1918).

[3] See Harned, *Loc. cit.*

[4] *Loc. cit.*