

The Destructive and Preservative Effects of Neutral Salts upon Hide Substance—II^{1,2}

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IN A previous paper³ certain peculiar differences in the hydrolytic catalysis of hide powder by salts were revealed. The alkali and alkaline-earth halides exerted a strong hydrolytic action, the latter much more than the former, iodide and bromide much more than chloride, while the sulfates of sodium and magnesium were shown to exert marked inhibition to the destructive action of water on hide substance. These experiments were conducted in a manner such as to exclude bacterial action. While not identical in all respects, the results obtained closely resembled the effect of salts in increasing the solubility of certain amino acids in water.⁴

In this investigation there is included the effect of (1) saturated solutions of some of the more common salts at three temperatures, (2) saturated solutions of sodium chloride-sodium sulfate mixtures at two temperatures, and (3) saturated sodium chloride solutions containing calcium chloride.

Fifty-gram portions of American standard hide powder were covered with 1-liter portions of the chemically pure salt solutions in stoppered bottles. In view of the danger of complications through bacterial action in the distilled water control, it was covered with toluene as inhibitory agent. Toluene was not added to the saturated salt solutions. The bottles were stored in the dark at the temperatures noted. They were shaken once daily during the first 4 weeks, and thrice or twice weekly thereafter. At the intervals of time noted in the tables, specimens of the solutions were withdrawn by pipet, filtered through dry ordinary filter papers, and a measured portion of the filtrates was subjected to the Kjeldahl process for determination of nitrogen. From the figures so obtained the percentage of hydrolysis of the hide powder was calculated. Corrections for the decrease in volume caused by these withdrawals were made in all subsequent calculations. There was none of the familiar evidence of bacterial action in any case.

Effect of Saturated Solutions of Various Salts

The salts listed in Table I were used. Saturated solutions at the three temperatures—7° C. (45° F.), room temperature 20–25° C. (68–77° F.), and 37.5° C. (99° F.)—were prepared

¹ Presented before the Division of Leather and Gelatin Chemistry under the titles "Hydrolysis of Hide Powder by Saturated Salt Solutions," by A. W. Thomas, and "Hydrolysis of Hide Powder by Saturated Mixtures of Sodium Chloride and Sodium Sulfate" by M. W. Kelly at the 72nd Meeting of the American Chemical Society, Philadelphia, Pa., September 5 to 11, 1926.

² Contribution No. 533 from the Chemical Laboratories, Columbia University.

³ Thomas and Foster, *THIS JOURNAL*, **17**, 1162 (1925).

⁴ Pfeiffer and Würigler, *Z. physiol. Chem.*, **97**, 128 (1916).

Solutions saturated with varying mixtures of sodium chloride and sodium sulfate show less catalysis of hydrolysis of hide powder than sodium chloride alone. At room temperature a solution saturated with a salt mixture in the proportion of 5 mols NaCl to 1 mol Na₂SO₄ preserves hide powder about as well as one saturated with sodium sulfate. Saturated sodium sulfate solutions show better antihydrolytic action at high temperatures than at low temperatures for the reason that at higher temperatures much more sodium sulfate is contained in a saturated solution. Calcium chloride is very destructive in its action. Sodium chloride also catalyzes the hydrolysis, but to a much less extent. When these salts are mixed together, the hydrolytic action is much less than with sodium chloride alone. In other words, the addition of calcium chloride to sodium chloride renders the latter a better hide preservative.

in each instance. While the pH values of saturated salt solutions may be of doubtful value, the same were measured and are entered here as a matter of record. The pH values of the solutions diluted ten times are likewise given.

These figures lead to the conviction that differences in hydrolytic action of the salts are not pH effects.

The results of the analyses are recorded in Table II and shown graphically in Figure 1.

The expected increased hydrolysis due to rise in temperature is shown in all cases except sodium sulfate. Exami-

nation of the results found for this salt, especially for the longer digestive periods, shows the hydrolysis order to be 7° C. > room temperature > 37.5° C., the degree of hydrolysis at the latter temperature being practically zero. This anomaly is explained upon consideration of the concentrations of sodium sulfate in solutions saturated at the three temperatures. The saturated solution at 37.5° C. contains almost twice as much sodium sulfate as that saturated at room temperature and about seven times that of the 7° C. saturated solution. Since the hydrolytic action is practically zero in the warm saturated solution, containing seven times as much of the salt as in the cold saturated solution in which hydrolysis was appreciable, conclusive corroboration of the statement made in the first paper³ is found—i. e., sodium sulfate is a hide preservative. This salt is an anticatalyst to hydrolytic action. It is to be emphasized at this point also that no antiseptic means other than sodium sulfate were used.

Table I—Salt Solutions Employed

SALT	PH OF SATURATED SOLUTION	PH OF DILUTE SOLUTION
NaCl	4.6	5.0
KCl	5.6	5.3
CaCl ₂	3.6	4.9
MgCl ₂	3.4	5.0
Na ₂ SO ₄	5.0	5.5

McLaughlin and Theis⁵ have corroborated the writers' earlier findings that sodium sulfate incites less hydrolysis of hide substance than sodium chloride. They criticize Thomas and Foster's suggested use of Glauber's salt instead of common salt for the commercial salting of hides as of a "highly speculative nature" and show that sodium sulfate is not a good antiseptic. Their paper shows that bacteria grow in saturated sodium sulfate solutions in contact with hide substance at 20° C. It is hoped that they will repeat their measurements at 37.5° C., since the present writers are convinced of the absence of bacteria in saturated solutions of the sulfate at this temperature.

The digestions at the lower temperatures also appeared to be free from organisms, but the results of McLaughlin and

⁵ *Collegium*, No. 678, 431 (1926).

Theis are to be accepted as more accurate since they made actual bacterial counts. They insist upon the continued use of sodium chloride as a hide preservative.

Table II—Per Cent Hydrolysis of Hide Powder

TIME	NaCl	KCl	CaCl ₂	MgCl ₂	Na ₂ SO ₄	WATER
<i>Days</i>						
TEMPERATURE, 7° C. (45° F.)						
7	...	1.0	14	12	0.0	...
14	0.7	1.3	15	15	0.0	0.7
21	1.3	1.3	15	15	0.8	0.8
28	1.5	1.3	15	16	1.0	1.1
42	1.3	1.4	15	16	0.8	...
88	2.3	2.2	15	18	1.6	1.3
171	3.7	4.1	18	21	6.1	3.0
ROOM TEMPERATURE						
7	6	8	18	21	0.4	5.2
14	10	12	19	24	0.4	6.3
21	11	13	20	24	0.5	7.2
28	14	16	22	27	0.8	8.2
42	17	18	...	29	1.2	8.6
88	24	22	27	36	4.3	9.5
171	30	24	33	48	6.8	10.3
TEMPERATURE, 37.5° C. (99° F.)						
4	10	15	20	26	0.4	14
8	15	22	22	30	0.6	21
12	16	25	...	30
19	...	29	24	35	...	24
26	29	36	30	41	0.6	...
33	31	35	30	...	0.8	28
40	35	36	35	49	1.0	28
89	45	36	38	28
172	50	37	55	82	0.7	32

The data in Table II and Figure 1 show that magnesium chloride is the most destructive of the salts tried, its hydrolytic promoter action being most marked at the higher temperatures; over 80 per cent of the hide powder is hydrolyzed at 37.5° C. in 6 months. With the exception of the action at 7° C., it is seen that sodium chloride promotes hydrolysis to nearly the same extent as calcium chloride.

The greater dissolving power of magnesium chloride is in

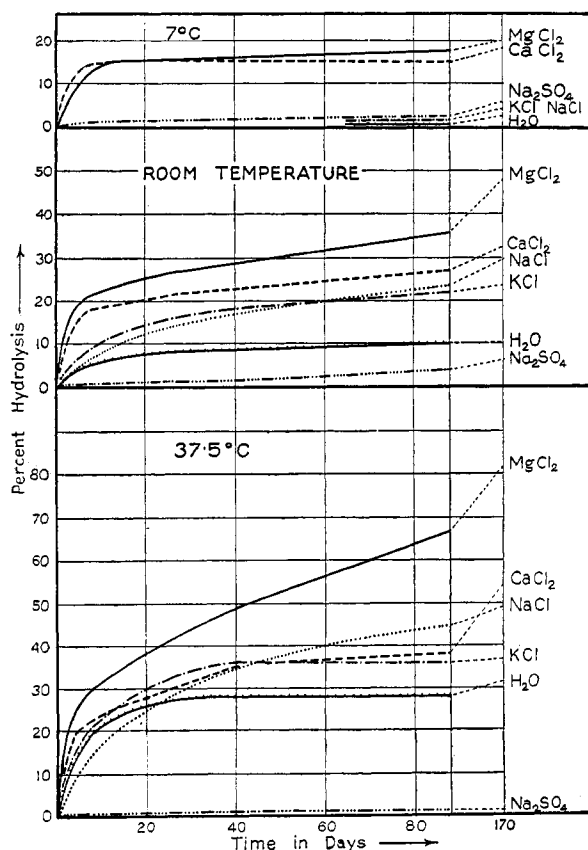


Figure 1—Hydrolysis of Hide Powder in Saturated Salt Solutions at Different Temperatures

harmony with the results of Howe,⁶ who found that calcium chloride is a better precipitant of the proteins of blood serum than magnesium chloride.

Effect of Presence of Calcium Chloride in Saturated Sodium Chloride Solutions

Thomas and Foster,³ impressed by the destructive property of calcium and magnesium chlorides, implied that the presence of these salts in commercial salt might be prejudicial to proper hide conservation. To test this supposition, the effect of the addition of calcium chloride to sodium chloride was measured.

Saturated solutions of sodium chloride were prepared at room temperature, and to each was added the required amount of a concentrated solution of calcium chloride to give desired concentrations of this salt. Since sodium chloride is precipitated from its saturated solution by calcium chloride,⁷ it was assumed that each final mixed solution was saturated with respect to sodium chloride. The resulting solutions were analyzed for their calcium and chloride contents, from which the results in Table III were calculated.

Table III—Composition of Saturated Sodium Chloride-Calcium Chloride Solutions

No.	SALT IN SALT MIXTURE		MOLAR CONCENTRATION	
	NaCl	CaCl ₂	NaCl	CaCl ₂
	<i>Per cent by weight</i>		<i>Mols</i>	<i>Mols</i>
1	100	0	5.41	0
2	99.9	0.1	5.41	0.003
3	99.5	0.5	5.37	0.015
4	99.0	1.0	5.32	0.030
5	97.9	2.1	5.19	0.058
6	97.0	3.0	5.11	0.084
7	84.8	15.2	4.01	0.38

The hide powder was subjected to the action of these solutions as previously described for the other salts, with the unexpected results as shown in Table IV and Figure 2.

Table IV—Per Cent Hydrolysis of Hide Powder in Saturated Solutions of Sodium Chloride Containing Calcium Chloride

TIME	SOLUTION NUMBER						
	1	2	3	4	5	6	7
<i>Days</i>							
7	5.5	5.1	4.8	4.6	4.0	3.6	1.6
14	6.2	6.0	5.5	5.1	4.4	3.9	2.0
28	8.0	7.8	7.1	6.8	5.8	4.9	2.1
30
56	13.3	11.8	11.7	11.4	9.7	8.1	3.3
112	23.3	21.2	20.6	18.6	16.1	13.7	4.0

The striking fact here is that mixtures of sodium chloride and calcium chloride are less destructive than either alone, or that, while calcium chloride alone is more destructive in its action than sodium chloride, its addition to saturated solutions of sodium chloride produces solutions which are good hide preservatives. This is an example of what the biologists call "antagonistic salt action." Upon perusal of the literature a case resembling this is found in the work of Fenn,⁸ who found that, when either sodium or calcium chloride is present in an aqueous gelatin solution, more alcohol is required to precipitate the gelatin than in the absence of these salts. When sodium and calcium chlorides are present, especially in the ratio of 100 mols NaCl to 8 mols CaCl₂, it takes less alcohol to precipitate the gelatin; in other words, gelatin is less soluble in a solution of a mixture of these salts than in either singly.

Apparently, then, the presence of small amounts of calcium chloride in commercial salt is indicated to be an advantage rather than a disadvantage for salting hides.

⁶ *J. Biol. Chem.*, **57**, 241 (1923).

⁷ Cameron, Bell, and Robinson, *J. Phys. Chem.*, **11**, 396 (1907).

⁸ *J. Biol. Chem.*, **34**, 141 (1918).

Effect of Saturated Mixtures of Sodium Chloride and Sodium Sulfate

In anticipation of criticism of the suggested use of sodium sulfate in commercial hide salting, arising from the cost of this salt, especially for saturating hides at tropical temperatures, an investigation of the effects of solutions saturated with mixtures of the chloride and sulfate was undertaken.

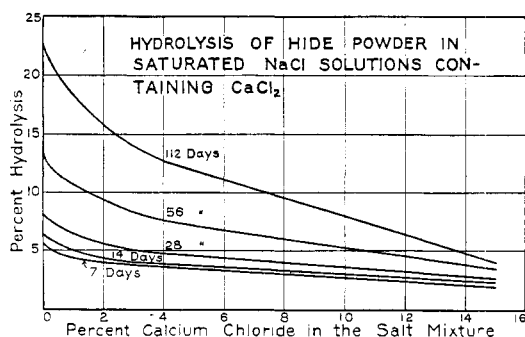


Figure 2

The preparation of solutions saturated with respect to both sodium chloride and sulfate and to varying ratios of the two would require considerable experimentation, but fortunately the information is available in the data of Seidell.⁹ These data served as a valuable guide in preparing the solutions which were saturated at room temperature and at 37.5° C. All the solutions were analyzed for chloride and sulfate, from which the data given in Table V were calculated.

Table V—Composition of Saturated Solutions

No.	SALT IN SALT MIXTURE		MOLAR CONCENTRATION	
	NaCl	Na ₂ SO ₄	NaCl	Na ₂ SO ₄
ROOM TEMPERATURE				
	Per cent by weight		Mols	
1	0.0	100.0	0.00	1.46
2	37.0	63.0	1.48	1.03
3	61.5	38.5	2.93	0.75
4	63.1	36.9	3.37	0.81
5	67.2	32.8	4.14	0.83
6	71.5	28.5	4.41	0.73
7	76.1	23.9	4.79	0.62
8	79.3	20.7	4.86	0.52
9	86.8	13.2	5.05	0.32
10	91.8	8.2	5.15	0.19
11	100.0	0.0	5.29	0.00
TEMPERATURE, 37.5° C.				
12	0.0	100.0	0.00	2.91
13	5.6	94.4	0.40	2.76
14	12.4	87.6	0.84	2.43
15	21.2	78.8	1.34	2.05
16	37.9	62.1	2.28	1.54
17	54.1	45.8	3.18	1.11
18	70.3	29.7	4.13	0.72
19	80.6	19.4	4.98	0.49
20	88.5	11.5	5.19	0.28
21	100.0	0.0	5.46	0.00

The hydrolytic effect of the saturated solutions of the above mixtures upon hide powder at various intervals of time are given in Tables VI and VII, and in Figures 3 and 4. The technic employed was identical to that already described in this paper.

No antiseptic was employed. Bacterial action was not apparent in any case. Mold appeared in two cases, in the solution containing saturated sodium sulfate and the one containing 63 per cent sulfate and 37 per cent chloride in the salt mixture, at room temperature and at the time of 350 days.

All mixtures of the two salts are seen to cause less hydrolytic action than sodium chloride alone. This is especially marked at the higher temperature. There is no straight-line decrease from the high hydrolytic action of sodium chloride to the low hydrolytic (or preservative) action of sodium sulfate, the

curve at room temperature decreasing to a minimum, followed by a rise before the final drop as a function of increasing sulfate and decreasing chloride concentration. Considering the degrees of hydrolysis over the period from 7 to 42 days, it is seen that the optimal preservative effect of a mixture of the two salts is obtained with the ratio of 5 mols chloride to 1 mol sulfate. It is significant here to refer again to the experiments of Fenn⁸ upon the amounts of alcohol required to precipitate gelatin from aqueous solutions in the presence of salts. He found that in the presence of the chloride and sulfate of sodium, the least amount of alcohol was required when the ratio of chloride to sulfate was 5 mols to 1 mol—i. e., gelatin was least soluble in a solution containing this ratio of these two salts. (Fenn used dilute, not saturated solutions of the salts.)

Table VI—Per Cent of Hide Powder Hydrolyzed at Room Temperature in Saturated Solutions of Mixtures of NaCl and Na₂SO₄

No.	SOLUTION		TIME IN DAYS								
	NaCl	Na ₂ SO ₄	7	14	21	28	35	42	91	182	350
Per cent											
1	0.0	100.0	0.8	...	1.2	1.9	3.2	3.8	6.3	7.3	8.2
2	37.0	63.0	0.9	2.5	3.5	4.4	6.9	8.5	9.7	15.3	18.9
3	61.5	38.5	1.3	2.3	3.6	4.7	6.1	6.5	9.3	12.1	12.3
4	63.1	36.9	1.0	1.9	2.9	4.2	5.3	5.8	10.3	13.6	14.1
5	67.2	32.8	0.8	1.3	2.0	2.9	3.8	4.4	9.1	15.1	17.1
6	71.5	28.5	1.0	1.7	2.3	3.4	4.4	5.1	9.5	16.6	...
7	76.1	23.9	1.1	1.7	2.4	3.6	4.5	5.2	10.3	17.0	19.8
8	79.3	20.7	1.4	2.4	3.5	4.7	6.0	6.7	11.8	19.2	19.5
9	86.8	13.2	2.9	3.5	6.2	7.6	9.4	10.5	16.5	22.9	24.4
10	91.8	8.2	4.2	...	8.2	9.8	12.4	13.2	18.5	25.3	26.0
11	100.0	0.0	6.7	9.4	11.3	13.5	16.4	17.7	...	29.8	30.6

Table VII—Per Cent of Hide Powder Hydrolyzed at 37.5° C. in Saturated Solutions of Mixtures of NaCl and Na₂SO₄

No.	SOLUTION		TIME IN DAYS					
	NaCl	Na ₂ SO ₄	7	14	28	56	112	160
Per cent								
12	0.0	100.0	...	0.5	0.6	...	0.5	0.8
13	5.6	94.4	...	0.4	0.5	...	0.6	0.9
14	12.4	87.6	...	0.5	...	0.5	0.7	1.0
15	21.2	78.8	...	0.6	...	0.5	0.8	1.2
16	37.9	62.1	...	0.6	0.7	1.1	2.2	3.0
17	54.1	45.8	1.0	1.2	1.4	2.5	5.0	7.3
18	70.3	29.7	1.8	2.3	3.6	6.5	12.3	16.6
19	80.6	19.4	2.2	2.8	4.4	7.5	13.6	18.9
20	88.5	11.5	4.3	6.2	10.0	15.7	26.1	31.8
21	100.0	0.0	12.7	14.7	27.4	37.6	52.2	51.7

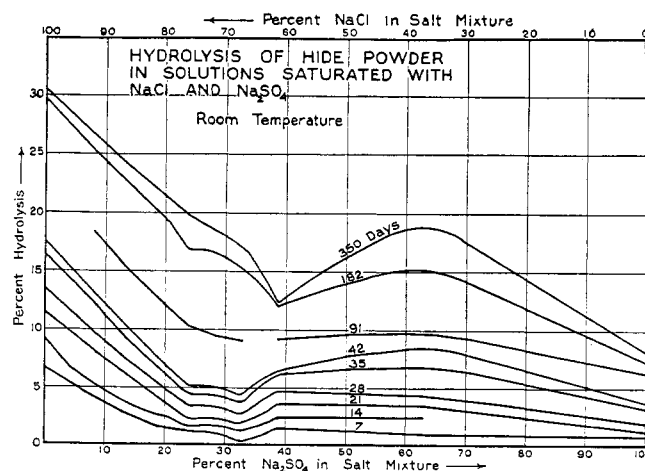


Figure 3

In the longer periods of 6 to 12 months, the minimum point for mixtures shifts to 4 mols chloride to 1 of sulfate. Beyond this ratio the hydrolytic action rises to a point which, in the absence of sufficient data, may only be estimated to be at the ratio of 3 mols chloride to 1 sulfate for periods less than one month, and 1.5 chloride to 1 sulfate for longer periods. In view of this fact it is obvious that any haphazard mixture of the two salts cannot be employed for salting hides at temper-

⁹ Am. Chem. J., 27, 55 (1902).

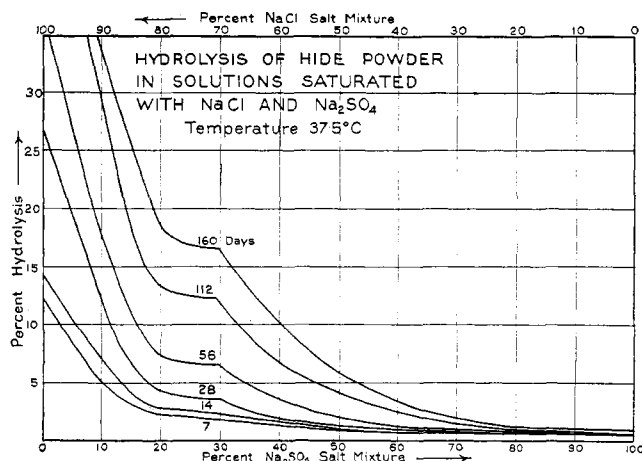


Figure 4

atures around 20–25° C. (68–77° F.). The best mixture is 4 or 5 mols of chloride to 1 of sulfate, which in fact is almost as good a preservative as pure sodium sulfate.

At 37.5° C. (99° F.) the picture is much less complicated. No matter what the ratio of sulfate to chloride happens to be, the more sulfate present the better is the preservative action. It is of practical value to note that up to one-fifth part by weight sodium chloride in the salt mixture the preservative action is almost as good as with sodium sulfate alone.

Since alkali sulfates are much more powerful precipitants of proteins from aqueous solutions than are the chlorides, the converse—namely, the greater “dissolving” action of chloride on hide substance and the greater antihydrolytic action of sulfate—might be expected.

Stiasny and Das Gupta¹⁰ have found that a jelly of isoelectric gelatin dissolves in solutions of sodium chloride, chlorate, nitrate and thiocyanate, while it shrinks in solutions of sodium sulfate.

Acknowledgment

The authors are indebted to A. F. Gallun and Sons Company for their aid in this investigation.

¹⁰ *Collegium*, 1925, 13.

Vapor-Composition Relationships in the System Bromine-Water^{1,2}

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DESPITE the importance of a knowledge of the vapor-composition relationships in the system bromine-water in connection with the rational design of equipment for the manufacture of bromine, no data on this subject appear in the literature. The present investigation was undertaken for the purpose of obtaining such data.

The bromine used was freed from organic compounds by distillation over potassium permanganate and strong sulfuric acid, and was then redistilled over potassium bromide to remove any traces of chlorine. The final distillation was made through a long Hempel column and only the middle fraction was collected for use.

Solution Having Single Liquid Layer

A solution prepared by dissolving some of this purified bromine in water was analyzed by treating a weighed portion with an excess of a solution of potassium iodide and titrating the liberated iodine with a standard solution of sodium thiosulfate. A weighed amount of the bromine solution (about 350 grams) was placed in a distilling flask (A in Figure 1) and was boiled until a suitable amount of distillate was obtained. During the distillation the asbestos oven surrounding the flask was kept slightly above the boiling point of the solution so as to prevent condensation and consequent fractionation in the upper part of the flask. The distillate was collected in the absorption bulb, B, which contained a concentrated solution of potassium iodide. The weight of the distillate was determined by weighing the absorption bulb before and after the distillation. The bromine content was determined by titrating the liberated iodine with a standard

solution of sodium thiosulfate. After the distillation was completed a sample of the residual solution in the distilling flask was withdrawn and analyzed for bromine. From the data thus obtained the bromine content of the distillate and the average bromine content of the solution from which the distillate was derived were calculated. The results obtained were as follows:

GRAMS BROMINE IN 100 GRAMS			
Solution	Distillate	Solution	Distillate
0.200	39.48	1.94	91.1
0.400	59.7	2.10	93.2
0.695	72.1	2.16	92.85
1.02	81.5	2.29	96.0
1.38	88.35	2.85	97.6
1.59	92.1	3.14	97.7

Procedure with Two Liquid Phases

It was found that this method gave fairly consistent and satisfactory results as long as the solution in the flask contained a single liquid layer, but that when enough bromine was present to form a separate liquid phase the results were very erratic and inaccurate. When two liquid layers were

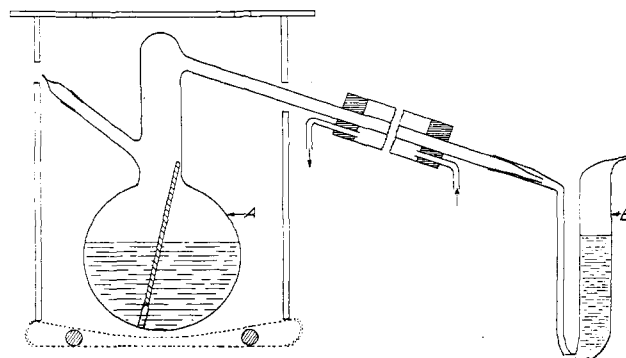


Figure 1

¹ Received January 10, 1927.

² This article is respectfully dedicated by the authors to Prof. L. M. Dennis, and will be reprinted as Article Number Four in the Louis Munroe Dennis Quarter Century Volume to be published in commemoration of the completion by Professor Dennis of twenty-five years of service as head of the Department of Chemistry of Cornell University.