[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, SYRACUSE UNIVERSITY.]

THE INFLUENCE OF GLUCOSE ON THE DIALYSIS OF SUCROSE THROUGH A PARCHMENT MEMBRANE. THE POSSIBILITY OF THE SEPARATION OF GLUCOSE FROM SUCROSE BY DIALYSIS.

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Introduction.

A study of the literature has shown that the separation of glucose from sucrose by dialysis has never been attempted. Pfeffer in his classical experiments[1] upon osmosis in vegetable cells discovered that the osmotic pressure of dilute sugar solutions was proportional to the concentration, and that the osmotic pressure of sugar solutions underwent a regular increase with increase of temperature. And in a practical way, Dubrunfaut devised the old osmose process[2] for recovering sucrose from beet molasses. If beet molasses be dialyzed by means of parchment paper against running water the salts will diffuse with much greater rapidity than the sucrose and in this way the percentage of melassigenic impurities can be considerably reduced; beet molasses thus purified will deposit upon evaporation crystals of sucrose up to the new saturation point for the solution of undialyzed impurities. This process has given place technically to the saccharate process of sucrose recovery.

O. A. Val'tera[3] has made use of the separation by dialysis in his study of enzymes.

In order to obtain information as to whether sucrose and glucose in mixtures could be separated by dialysis and what effect glucose had on the dialysis of sucrose, five different solutions, each containing a mixture of sucrose and glucose were dialyzed through parchment paper.

Experimental.

The materials to be dialyzed were sucrose and glucose, each containing less than 1% of impurities. Mixtures of sucrose and glucose were made up as follows: 2 g. each of sucrose and glucose in 100 cc. of distilled water; 10 g. of glucose and 25 g. of sucrose made up to 100 cc. with water; 5 g. of glucose and 25 g. of sucrose made up to 100 cc. with water; 0.5 g. of glucose and 25 g. of sucrose made up to 100 cc. with water. For the purpose of dialysis, 25 cc. of each of the above solutions was taken, and diluted to $^1/_4$ strength for dialysis.

The dialysis was made through a parchment paper membrane. The parchment tube was made about 12.5 cm. long and 5 cm. in diameter.

[1] Pfeffer's "Osmotische Untersuchungen," Leipzig, **1877**.

[2] C. A. Browne, "A Handbook of Sugar Analysis," J. Wiley and Sons Co., **1912**, p. 649.

[3] Val'tera, "A method of Dialysis of Enzymes," *Bull. Acad. Sci. Russ.*, **1917**, (6), No. 13, pp. 1075–88, abs. *Exper. Sta. Record*, **40**, 111 (1921).

A solid rubber stopper was fitted into one end of the parchment tube and cemented there with paraffin. Sealing wax was first used but it was found that the wax spread on hardening and caused leaks in the joints. A 1-holed rubber stopper was fitted into the other end of the parchment tube. The sugar solution was passed into the tube by means of a 25cc. pipet. The dialysis tube was then placed in a narrow beaker and 150 cc. of distilled water was run into the beaker, thus surrounding the parchment tube. Five-cc. portions of the solution were withdrawn, two at a time, at definite intervals and placed in test-tubes. At each removal, the sucrose in one of these samples was inverted by adding 5 drops of dil. hydrochloric acid.

Bertrand's method, with slight modifications, was used in analyzing the samples. Five cc. of copper sulfate solution (from 140 g. of pure copper sulfate pentahydrate dissolved in 1000 cc. of water) and 5 cc. of a solution made up of Rochelle salt and 150 g. of solid sodium hydroxide dissolved in 1000 cc. of water were added to each of the 5 cc. samples to be analyzed. The resulting solution was placed in a small beaker and boiled for 3 minutes. The solution was filtered through asbestos in a Gooch crucible and the precipitate of cuprous oxide was washed with distilled water. The asbestos film was transferred to a beaker and 30 cc. of hot water added. The Gooch crucible was rinsed out with a hot saturated solution of ferric sulfate in 20% sulfuric acid and the rinsing run into the beaker containing the precipitate. The cuprous oxide was changed to copper sulfate by the ferric sulfate solution, a corresponding amount of which was reduced to the ferrous state. The solution was now titrated with standard potassium permanganate. The ferrous sulfate was thus oxidized to the ferric condition. By calculation the amount of cuprous oxide precipitate was determined for each sample and from this the amount of sugar corresponding to the amount of precipitated copper.

The following tables and graphs show the results of the work. The dialysis was conducted at the temperature of the laboratory, about 22.5°.

Discussion of Results.

The results with these varying concentrations show that glucose dialyzed faster than sucrose. The influence of glucose on the dialysis of sucrose is of such a character as to keep the ratio of glucose to sucrose approximately constant after 3 hours of dialysis, irrespective of the concentration of the sucrose to be dialyzed. This can be plainly seen in Fig. 4. In Fig. 3 it is evident that the rate of the dialysis of glucose increases as the concentration of the glucose decreases, the concentration of the sucrose remaining the same.

The ratio of the percentage of the glucose to the percentage of the sucrose dialyzed is fairly constant, as seen in Tables I A, B and C, after 3 hours of dialysis; but on using a very small concentration of glucose, as in Table I D, the ratio increases approximately 2.0 times its former value.

The ratio of the dialysis of glucose to sucrose was found to be 2.5 to 1 respectively in solutions of glucose of 2% or greater; but in more dilute

TABLE IA.

RESULTS.

Original Solution: 2% Glucose and 2% Sucrose, 25 cc. was used for Dialysis.

Dialysis Solution: 0.5 g. of Glucose, 0.5 g. of Sucrose, Dialyzed into 150 cc. of Water.

Time of experiment after starting dialysis.	KMnO4 solution used.	Copper per 5 cc. of solution before inversion. (Due to glucose.)	Copper per 5 cc. of solution after inversion. (Due to glucose and inverted sucrose.)	Equivalent glucose per 5 cc. of solution.	Equivalent total invert sugar per 5 cc. of solution.	Invert sugar due to sucrose per 5 cc. of solution.	Sucrose per 5 cc. of solution. (Calc.).	Factor (dilution).	Total glucose dialyzed.	Total sucrose dialyzed.	Portion of original glucose dialyzed.	Portion of original sucrose dialyzed.	Approximate ratio glucose to sucrose dialyzed.
Hours.	Cc.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.		Mg.	Mg.	%.	%.	
0.75	(Lost)	....	....	....	....	....	....	30	....	....	....	....	....
0.75	0.60	....	5.01	....	2.43	....	....	30	....	....	....	....	....
1.50	0.72	6.01	....	2.91	....	0.05	....	28	81.48	1.33	16.30	0.27[a]	60.3
1.50	0.73	....	6.10	....	2.96	....	0.047	28	....	....	....	....	....
3.5	0.94	7.85	....	3.81	....	1.13	....	26	99.06	27.82	19.81[a]	3.96	5.0
3.5	1.22	....	10.19	....	4.94	....	1.07	26	....	....	....	....	....
4.5	(Lost)	....	....	....	....	....	....	24	....	....	....	....	....
4.5	(Lost)	....	....	....	....	....	....	24	....	....	....	....	....
6.5	1.20	10.02	....	4.86	....	2.75	....	22	106.92	....	21.38	....	1.8
6.5	1.88	....	15.70	....	7.61	....	2.61	22	....	57.42	....	16.48	....
0.5	0.30	2.51	....	1.22	....	0.48	....	30	36.60	....	7.32	....	....
0.5	0.42	....	3.50	....	1.70	....	0.46	30	....	13.80	....	2.76[a]	2.7
1.0	0.55	4.59	....	2.23	....	0.20	....	28	62.44	....	12.49	....	11.7
1.0	0.60	....	5.01	....	2.43	....	0.19	28	....	5.32	....	1.06	....
3.0	1.12	9.35	....	4.54	....	0.77	....	26	118.04	....	23.61	....	6.2
3.0	1.31	....	10.94	....	5.31	....	0.73	26	....	18.98	....	3.80	....
4.0	1.30	10.86	....	5.27	....	....	....	24	126.48	....	25.30	....	....
4.0	(Lost)	....	....	....	....	....	....	24	....	....	....	....	....
6.0	1.64	13.69	....	6.64	....	3.77	....	22	146.08	....	29.22	....	1.9
6.0	2.57	....	21.46	....	10.41	....	3.58	22	....	78.76	....	15.75	....

[a] Probable analysis error. The column headed "Factor (dilution)" gives the number by which the mg. of glucose and sucrose from 5 cc. of the solution must be multiplied to give the total mg. of glucose and sucrose represented in the solution in the beaker.

TABLE IB.

Original Solution: 10% Glucose and 25% Sucrose; 25 cc. was used for Dialysis.

Dialysis Solution: 2.5 g. of Glucose, 6. 25 g. of Sucrose, Dialyzed into 150 cc. Water.

0.5	0.42	3.50	....	1.70	....	1.36	....	30	51.0	....	2.04	....	3.3
0.5	0.75	....	6.30	....	3.06	....	1.29	30	....	38.7	....	0.62	...
1.0	0.62	5.20	....	2.52	....	2.67	....	28	70.56	....	2.82	....	2.5
1.0	1.28	....	10.70	....	5.19	....	2.54	28	....	71.12	....	1.13	...
2.0	1.05	8.77	....	4.25	....	4.74	....	26	110.50	....	4.42	....	2.4
2.0	2.22	....	18.54	....	8.99	....	4.50	26	....	117.0	....	1.87	...
3.0	1.43	11.94	....	5.79	....	6.45	....	24	138.96	....	5.56	....	2.4
3.0	2.98	....	24.88	....	12.24	....	6.13	24	....	147.12	....	2.35	...
4.5	1.82	15.20	....	7.37	....	9.14	....	22	162.14	....	6.49	....	2.1
4.5	3.98	....	33.23	....	16.51	....	8.68	22	....	190.96	....	3.06	...
5.5	3.18	26.55	....	13.02	....	16.38	....	20	260.40	....	10.42	....	2.1
5.5	6.97	....	58.20	....	29.40	....	15.56	20	....	311.20	....	4.97	...
7.0	3.37	28.14	....	13.92	....	21.69	....	18	250.56	....	10.02	....	1.7
7.0	8.33	....	69.55	....	35.61	....	20.61	18	....	370.98	....	5.93	...
24.5	8.27	69.05	....	35.40	....	25.15	....	16	566.4	....	22.65	....	3.7
24.5	13.59	....	113.47	....	60.55	....	23.89	16	....	382.24	....	6.11	...

TABLE IC.

Original Solution: 5% Glucose and 25% Sucrose; 25 cc. was used for Dialysis.

Dialysis Solution: 1.25 g. of Glucose, 6.25 g. of Sucrose, Dialyzed into 150 cc. Water.

Time, drawn out after starting dialysis.	$KMnO_4$ solution.	Copper per 5 cc. of solution before inversion. (Due to glucose.)	Copper per 5 cc. of solution after inversion. (Due to glucose and inverted sucrose.)	Equivalent glucose per 5 cc. of solution.	Equivalent total invert sugar per 5 cc. of solution.	Invert sugar due to sucrose per 5 cc. of solution.	Sucrose per 5 cc. of solution. (Calculated.)	Factor (dilution).	Total glucose dialyzed.	Total sucrose dialyzed.	Portion of original glucose dialyzed.	Portion of original sucrose dialyzed.	Approximate ratio glucose to sucrose dialyzed.
Hours.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.	Mg.		Mg.	Mg.	%.	%.	
0.5	0.41	3.4	....	1.65	....	2.47	....	30	49.50	70.50	3.96	....	3.5
0.5	1.02	....	8.5	....	4.12	....	2.35	30	....	....	....	1.13	...
1.0	0.65	5.4	....	2.62	....	2.47	....	28	73.36	....	5.87	....	4.9
1.0	1.80	....	10.5	....	5.09	....	2.35	28	....	75.80	....	1.21	...
2.0	0.98	8.18	....	3.97	....	9.86	....	26	103.32	....	8.27	....	2.1
2.0	3.35	....	27.97	....	13.83	....	9.37	26	....	243.62	....	3.90	...
3.0	1.48	12.35	....	5.99	....	12.74	....	24	143.76	....	11.50	....	2.5
3.0	4.50	....	37.57	....	18.73	....	12.10	24	....	290.40	....	4.65	...
4.5	2.25	18.78	....	9.11	....	18.83	....	22	200.42	....	16.03	....	2.5
4.5	6.64	....	55.4	....	27.94	....	17.89	22	....	393.58	....	6.30	...
5.5	2.55	21.29	....	10.43	....	24.59	....	20	208.60	....	16.69	....	2.2
5.5	6.64	....	68.55	....	35.02	....	23.36	20	....	467.20	....	7.48	...
7.0	2.21	18.45	....	8.95	....	27.05	....	18	161.10	....	12.89	....	1.8
7.0	8.42	....	70.31	....	36.00	....	25.70	18	....	462.60	....	7.40	...
24.5	5.02	41.9	....	21.00	....	44.73	....	16	336.00	....	26.88	....	2.5
24.5	14.62	....	122.1	....	65.73	....	42.49	16	....	679.84	....	10.88	...

TABLE ID.

Original Solution: 0.5% Glucose and 25% Sucrose, 25 cc. was used for Dialysis.

Dialysis Solution: 0.125 g. of Glucose and 6.25 g. of Sucrose, Dialyzed into 150 cc. of Water.[1]

0.5	0.20	1.67	....	0.71	....	2.53	....	30	21.30	72.00	17.04	....	14.8
0.5	0.80	....	6.68	....	3.24	....	2.40	30	....	....	....	1.15	....
1.0	0.25	2.09	....	1.02	....	4.85	....	28	28.56	129.08	22.84	....	11.0
1.0	1.45	....	12.11	....	5.87	....	4.61	28	....	....	....	2.07	....
2.0	0.27	2.25	....	1.09	....	9.24	....	26	28.34	228.28	22.67	....	6.2
2.0	2.55	....	21.29	....	10.33	....	8.78	26	....	....	....	3.65	....
3.0	0.37	3.09	....	1.50	....	13.53	....	24	36.00	308.40	28.80	....	5.8
3.0	3.66	....	30.56	....	15.03	....	12.85	24	....	....	....	4.93	....
4.5	0.41	3.40	....	1.65	....	20.04	....	22	36.30	418.88	29.04	....	4.3
4.5	5.22	....	43.59	....	21.69	....	19.04	22	....	....	....	6.70	....
5.5	0.45	3.76	....	1.82	....	23.37	....	20	36.40	444.00	29.12	....	4.1
5.5	6.01	....	50.18	....	25.19	....	22.20	20	....	....	....	7.10	....
7.0	0.55	4.59	....	2.23	....	21.44	....	18	40.14	366.66	32.11	....	5.5
7.0	5.67	....	47.37	....	23.67	....	20.37	18	....	....	....	5.87[b]	....
24.5	1.15	9.60	....	4.66	....	49.12	....	16	74.56	746.56	59.65	....	5.0
24.5	12.19	....	101.78	....	53.78	....	46.66	16	....	....	....	11.94	....

[b] Probable slight analytical error.

solutions of glucose (0.125%), the ratio of the dialysis of glucose to sucrose was approximately 2.0 times as much or approximately 5.0 to 1, respectively.

TABLE II.

COMPARISON OF RESULTS.

Time.	Glucose Orig. in Tube, Dialyzed. Tables.			Sucrose Orig. in Tube, Dialyzed. Tables.			Approx. Ratio of Glucose to Sucrose Dialyzed. Tables.		
Hours.	I B. %.	I C. %.	I D. %.	I B. %.	I C. %.	I D. %.	I B.	I C.	I D.
0.5	2.04	3.96	17.04	0.62	1.13	1.15	3.3	3.5	14.8
1.0	2.82	5.87	22.84	1.13	1.21	2.07	2.5	4.9	11.0
2.0	4.42	8.27	22.67	1.87	3.90	3.65	2.4	2.1	6.2
3.0	5.56	11.50	28.80	2.35	4.65	4.93	2.4	2.5	5.8
4.5	6.49	16.03	29.04	3.06	6.30	6.70	2.1	2.5	4.3
5.5	10.42	16.69	29.12	4.97	7.48	7.10	2.1	2.2	4.1
7.0	10.02	12.89	32.11	5.93	7.40	5.87	1.7	1.8	5.5
24.5	22.65	26.88	59.65	6.11	10.88	11.94	3.7	2.5	5.0
					Average[a]		2.5	2.8	7.1

[a] The average is rather constant if the figures *after 3 hours of dialysis* are taken. In the case of the average after 3 hours of dialysis, we have for Table I B:—2.4; I C:—2.5, and ID:—4.7; and if we take the average after 3 hours of dialysis for Table I A probable experimental errors excluded, we have 2.0 for the approximate ratio of glucose to sucrose dialyzed.

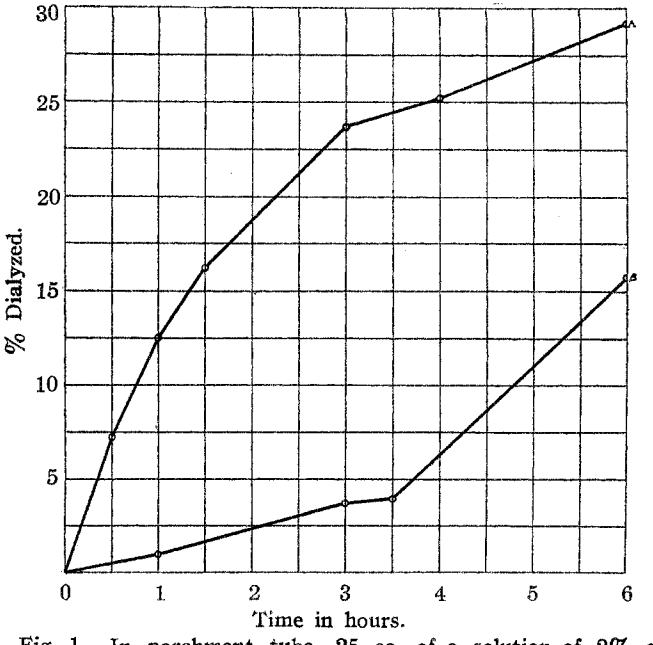

Fig. 1.—In parchment tube, 25 cc. of a solution of 2% of glucose and 2% of sucrose; dialyzed into 150 cc. of water.

A = % of the glucose dialyzed; B = % of the sucrose dialyzed.

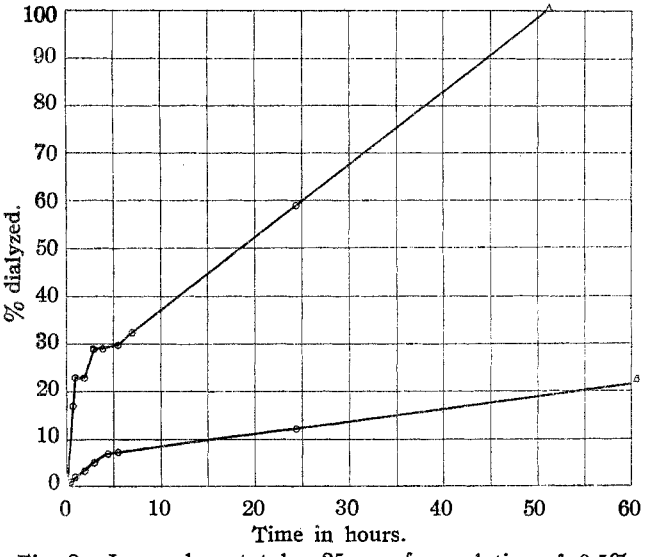

Fig. 2.—In parchment tube, 25 cc. of a solution of 0.5% of glucose and 25% of sucrose; dialyzed into 150 cc. of water.
A = % of the glucose dialyzed; B = % of the sucrose dialyzed.

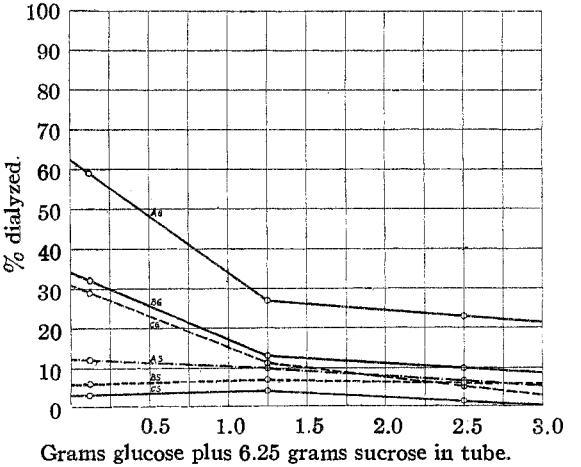

Fig. 3.—*AG* = % of glucose dialyzed in 24.5 hours; *BG*, in 7.0 hours; *CG*, in 3.0 hours.
AS = % of sucrose dialyzed in 24.5 hours; *BS*, in 7.0 hours; *CS*, in 3.0 hours.

It is shown that in very dilute mixtures of glucose and sucrose, the former can be separated qualitatively from the latter by dialysis in about 51 hours (see Fig. 2). There is a possibility of a quantitative separation of glucose from sucrose by fractional dialysis.

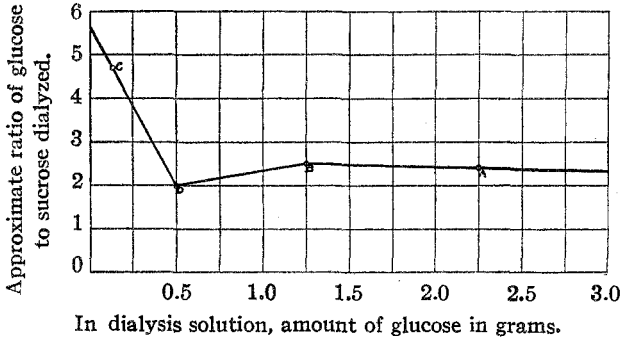

Fig. 4.—*A* represents 25 cc. of a solution of 10% of glucose and 25% of sucrose, dialyzed into 150 cc. of water through a parchment membrane; average after 3 hours of dialysis.
B = 25 cc. of a solution of 5% of glucose and 25% of sucrose;
C = 25 cc. of a solution of 0.5% of glucose and 25% of sucrose;
D = 25 cc. of a solution of 2% of glucose and 2% of sucrose.

Summary.

1. Five mixtures of sucrose and glucose solutions were dialyzed through parchment paper under standardized conditions and the following general facts developed as a result of the data obtained.

(*a*) The percentages of glucose and sucrose dialyzed in mixtures of solutions of these two substances vary inversely as the concentrations in the original solutions.

(*b*) In mixtures of glucose and sucrose, the influence of glucose on the dialysis of sucrose is of such a character as to keep the ratio of glucose to sucrose dialyzed approximately constant, irrespective of the concentration of the sucrose to be dialyzed, provided that the concentration of the glucose is not less than 2%, and the time of dialysis has exceeded 3 hours. In dialysis of solutions of less than 2% glucose, the glucose dialyzes much faster than at the above rate, and in 0.125% glucose solution the rate of the percentage of the glucose to that of the sucrose dialyzed is 5.0 to 1, respectively, this being 2.0 times as great a rate as in solutions of 2% or more glucose. Hence, glucose dialyzes faster than sucrose.

(*c*) In very dilute mixtures of glucose and sucrose, the former can be separated qualitatively from the latter by dialysis in about 51 hours. There is a possibility of a quantitative separation of glucose from sucrose by fractional dialysis.

(*d*) The above results apply to dilute solutions within the range covered by the experimental work.

2. The rate of dialysis was determined by removing definite volumes of the dialyzed solution at recorded intervals and inverting one portion of the removed samples to determine the percentage of sucrose calculated from the portion that was inverted.

3. Bertrand's method of analysis was used.

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SYMMETRICAL DI-ISOPROPYL-HYDRAZINE AND ITS DERIVATIVES.

(Preliminary Article.)

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Introduction.

Little work has been done on the purely aliphatic symmetrical hydrazines or hydrazo compounds and, with the exception of the stable azomethane[1] and certain azo derivatives of *iso*butyric acid,[2] the corresponding azo derivatives are unknown. Harries[3] could not isolate azoethane, and Franke[4] who obtained a small amount of symmetrical di-*iso*butyl-hydrazine, evidently did not have enough material to study this compound at all thoroughly. Busch, in working with the latter hydrazine[5] does not mention the azo compound. He reports that Stolle and his coworkers made symmetrical hydrazines, but there seem to be no published articles available on this work.

The azines which are so easily prepared from hydrazine through its reaction with aldehydes and ketones, both aliphatic and aromatic, might be expected to yield, on reduction, the corresponding hydrazo compounds and thus furnish a readily available source for these substances. In some cases the reduction proceeds smoothly; *e. g.*, symmetrical benzyl-hydrazine ($C_6H_5CH_2NHNHCH_2C_6H_5$) is easily prepared from benzalazine, ($C_6H_5CH=N-N=CH-C_6H_5$). However, up to the present the reduction, in this sense, of aliphatic aldazines and ketazines has failed. Curtius, who discovered dimethyl-ketazine[6] ($(CH_3)_2>C=N-N=C$

[1] Thiele, *Ber.*, **42**, 2575 (1909).

[2] Thiele and Heusser, *Ann.*, **290**, 30 (1896). Thiele and Stange, *Ann.*, **283**, 1 (1894). Bailey and Knox, THIS JOURNAL, **29**, 890 (1907).

[3] Harries, *Ber.*, **27**, 2279 (1894).

[4] Franke, *Monatsh.*, **19**, 526 (1898).

[5] August Busch, "Uber Isobutylhydrazine und Diisobutylhydrazine," *Dissertation*, Heidelberg, **1904**.

[6] Curtius, *J. prakt. Chem.*, [2] **44**, 164 (1891).