solid was at once powdered and preserved in glass stoppered bottles until analyzed. The preceding table gives the constituents of the ash of the leaf and of the bulb.

LARAMIE, WYOMING.

A STUDY OF THE VELOCITY OF REACTION BETWEEN PHENOL AND FORMALDEHYDE.

BY BENJAMIN JABLONOWER.

Received March 25, 1911.

Introductory.—Of late, great interest is being shown in the products resulting from the condensation reaction between phenols and formaldehyde or other compounds containing the methylene group (CH_2). This reaction has been carefully studied by many, and there is an extensive literature on the subject. Very careful descriptions are given of the product at different stages of the reaction. For example, Dr. L. H. Baekeland has pointed out that three separate and distinct forms of this condensation product are possible, *viz.*, a liquid or a fusible solid, soluble in alcohol (A), an infusible solid which softens at higher temperatures (B), and finally a hard insoluble infusible solid (C).[1] Descriptions of these are very minute and all the details of procedure to obtain them are carefully set forth. But nowhere in the literature on this subject, at least as far as the writer is aware, is there any mention of any attempt to study this reaction from a physico-chemical point of view. The following is an account of an effort to obtain data of such a character.

While preparing some of this condensation product by the action of formaldehyde solution on carbolic acid in the presence of a very small amount of ammonia, with the aid of heat, the writer noticed that the liquid became more and more viscous under the influence of the heat applied. The usual method of following the course of this reaction is to observe the fluidity or stickiness of the liquid. It occurred to the writer that it perhaps would be possible to make a more careful study of the reaction by regular periodic measurements of the viscosity. This, it was thought could be taken as a means for the determination of the velocity of the reaction. But it was found that this method was impracticable. However, the viscosity of a liquid, among other things, is dependent on the density. The viscosity, n, of a liquid flowing through a tube is given by the well known equation.

$$n = \frac{\pi r^4 p t}{8vl}, \text{ where}$$

r = the radius of the tube and

p = the pressure under which the volume, v, of liquid moves through the length, l, of the tube in the time, t.

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[1] L. H. Baekland, *J. Ind. Eng. Chem.*, 1, 149 (1909).

Now in the ordinary viscometer
$p = h \times d \times g$, where "h" is the difference in height between the columns of liquid in the two arms of the viscometer, "d" is the density of the liquid and "g" is the acceleration due to gravity. Hence,

$$n = \frac{\pi r^4 hdgt}{8vl}.$$

It is evident then that the viscosity is a regular function of the density or specific gravity. This last was the property chosen as the basis in the study of this condensation reaction, since it was found very convenient for regular periodic measurements.

The Apparatus and Method.—The vessels in which the reaction was allowed to proceed were large test tubes 12″ × 1$^1/_4$″, heat being applied by means of a water bath. Each of the test tubes contained a hydrometer (graduated to 0.001) and a thermometer for the observation of the temperature. The materials used were crystallin carbolic acid and a commercial 40% solution of formaldehyde. The use of commercial reagents, of course, introduces a grave source of error. The catalytic agent used was a normal solution of ammonium hydroxide, made up with tap water, since the use of distilled water would have been useless in view of the fact that the main reagents were subject to all the contaminations usually found in commercial formaldehyde and phenol.

The method of procedure consisted in heating the bath up to a given temperature, when the test tubes containing the solution of phenol in the formaldehyde solution, and a known per cent. of normal ammonia solution, were clamped in place. As soon as the temperature of the mixture had reached that of the bath, readings on the hydrometer were started and taken every ten minutes. This was usually continued for about seven hours, after which the tubes and their contents were allowed to cool with the bath. It must be pointed out here that the specific gravity at room temperature is inessential since the interest was centered upon the rise in this value with the time of heating rather than upon the actual specific gravity. In this way three series of measurements were made:

Series I—containing 1 part formaldehyde solution and 1 part carbolic acid by weight, or 1.3 mols of formaldehyde to 1 mol of phenol.

Series II—containing 2 parts formaldehyde solution and 1 part carbolic acid by weight, or 2.6 mols of formaldehyde to 1 mol of phenol.

Series III—containing 1 part formaldehyde solution and 2 parts of carbolic acid by weight, or 0.65 mols of formaldehyde to 1 mol of phenol.

In each of these series measurements were made upon solutions containing 2%, 4%, 6%, 8% and 10% of N NH_4OH measured by volume (0.065%, 0.13%, 0.195%, 0.26%, and 0.325% NH_3 by weight) at temperatures 65°, 70°, 75°, 85°, and 90° C. A normal solution of ammonium hydroxide was used as a conveniently dilute solution; for when a fairly concentrated solution was used, condensation took place immediately where the condensing agent came into contact with the mixture, thus making it impossible to obtain a homogeneous solution. The object of this investigation was to determin the influence upon the velocity of condensation exerted by: 1°— a change in the proportions of formaldehyde; 2°—increase in the percentage of catalytic or condensing agent; and 3°—increase of the temperature to which the mixture is heated. It is interesting to note here that no difficulties were experienced due to any water separated in the course of the reaction, since it was evaporated as fast as it was eliminated.

Before proceeding to a presentation of the observations a brief statement of the errors involved is perhaps pertinent:

1. The greatest and most serious error was the variation of the temperature. The bath used was provided with neither thermostat nor stirrer, and the thermometers used were graduated to 1°. Deviations as high as 2° C. were not uncommon.

2. The readings of the specific gravity were subject to error in that the hydrometers were graduated to read correctly at 20° C. Besides, calibration showed that the mean error in the readings was about 1% even at that temperature.

3. The possibility of error due to impurities in the materials used has been pointed out above.

The Observations.—The readings, taken at regular intervals, show that there is a gradual rise in the value of the specific gravity. The readings are not given here since there were so many, some 3600 in all. In order to facilitate the consideration of the observations curves were constructed

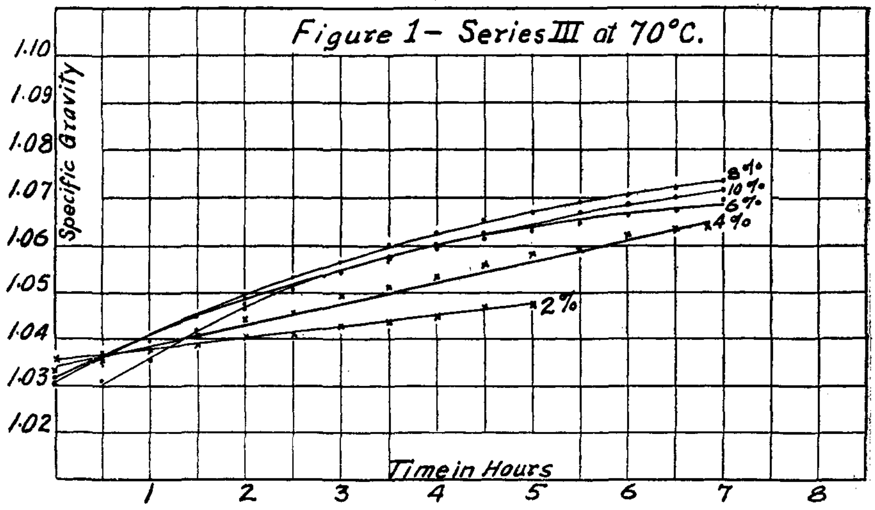


Figure 1— Series III at 70°C.

for each experiment with the time of heating in hours as abcissae and the specific gravity as ordinates. A few typical curves are shown in Figs. 1 and 2.

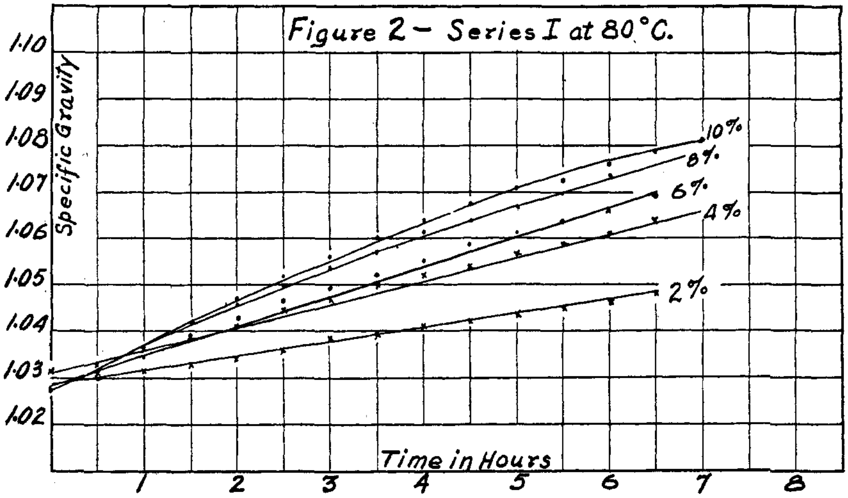


Figure 2— Series I at 80°C.

The figures show that there are two distinct cases:

1. The increase is regular and the graph obtained is a straight line.
2. The increase is not uniform and the graph obtained is a curve of decreasing slope.

Case 1.—Since this is represented by a straight line it is evident that the rate of increasing density is a constant. This constant can be calculated for each solution from the corresponding graph, for the slope of the line is given by the expression

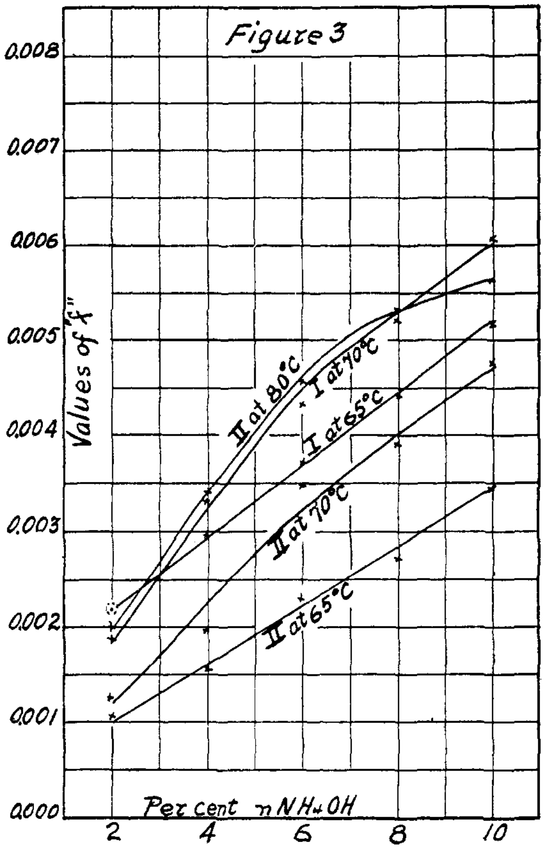
$$\text{Tan}\ \beta = \frac{s_2 - s_1}{t_2 - t_1},$$

where s_1 is the density at the time t_1 and s_2 is the density at the time t_2 which is $t_2 - t_1$ hours later. This may be written $\Delta s/\Delta t = k$ or $\Delta s = k\Delta t$, where "k" might be called the velocity constant for a given mixture heated at a given temperature.

On comparing the values of "k" (see tables given below) for a given solution heated at a given temperature, it is found that this constant increases with increasing percentage of ammonia; and within certain limits this increase is a proportionate one. In Fig. 3 are shown some of the curves obtained by taking the values of "k" as ordinates and the per cent. of N NH_4OH by volume as abcissas. Only a very few gave straight lines. By far the greater number gave curves resembling II at 70° and 80°; this shows that after a certain concentration of ammonia a further addition of the condensing agent is not followed by a porportionate rise in the velocity constant "*k*." By extrapolating these rather incomplete curves, it appears that after about 15%–20% *N* NH_4OH (or 0.5%–0.65% NH_4OH by weight) have been added additional ammonia leads to no further rise in the rate of increasing density. This behavior is not surprising since the ammonia is a catalytic agent and does not itself take part in the reaction. If we calculate the slope of the straight part of these curves, we obtain the value of the increase in the value of the velocity constant "*k*" per per cent. normal ammonia solution. Thus if *p* represents the per cent. *N* NH_4OH, we have

$$\frac{k_2 - k_1}{p_2 - p_1} = K_p.$$

The constant "K_p" might be termed the "per cent. coefficient" of the velocity constant "*k*."



Further, a comparison of the values of "*k*" for the same mixtures containing the same proportions of ammonia (see tables) reveals the fact that the velocity constant "*k*" rises with increasing temperature. In Fig. 4 are shown a few sample curves, constructed by taking the values of "*k*" as ordinates and the temperatures as abcissas. None of these graphs, as will be seen from the typical ones shown, are straight lines; they are all curves of increasing slope, indicating that the effect on "*k*" of rising temperature is greater at higher than at lower temperatures. However, they are nearly enough straight lines to make it possible to consider them so for the present, and to calculate their slope which is given by the expression

$$\frac{k_2 - k_1}{T_2 - T_1} = K_T,$$

where T_1 and T_2 are different temperatures. This constant "K_T", we might term the "temperature coefficient" of the velocity constant "*k*." In each series it was found that this value "K_T," was practically the same for all values of "*p*" or per cent. *N* NH_4OH. A peculiarity noticeable in these curves is that if we draw the best representative graphs we invariably obtain curves of the general form shown in Fig. 3 as a discontinuous line. The break in the curve may be more pronounced in some than in others, but it is present in all. No attempt is made here to offer any explanation. That can only come after a much more extensive study.

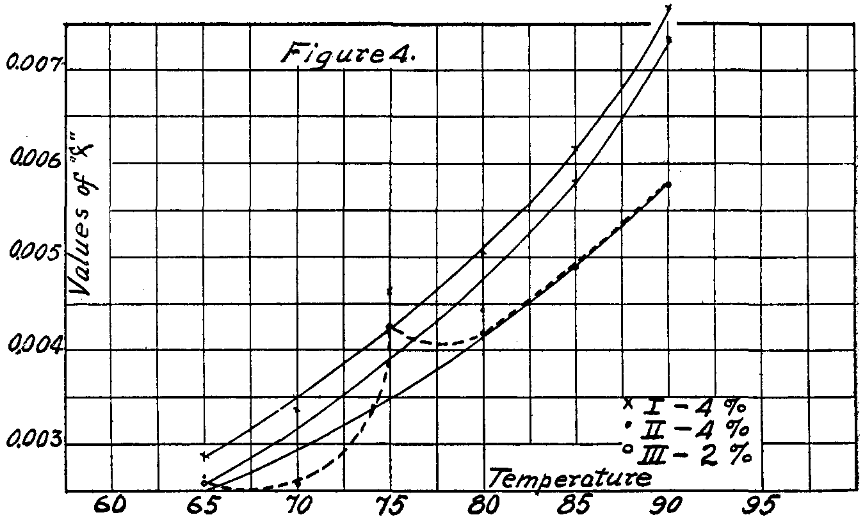


Figure 4.

Finally, it was found that with increasing temperature, the value of the "per cent. coefficient" (K_p) also rose. Whether or not this increase is proportional was not brought to light in the course of this investigation for reasons apparent from the tables below.

Case 2.—The fact of a curve of decreasing slope for all cases under this head makes it impossible to calculate a velocity constant for these mixtures. These curves were obtained in the cases of solutions either when the per cent. of ammonia exceeded a certain limit, usually 4%, or when the temperature was above a certain point, usually 75° (see tables). In each of these sub-series at a given temperature the curves tend to become straight towards the end, approaching a parallel to the straight line of highest slope in the sub-series. The limiting values for each of the series are:

SERIES I.—$k = 0.0060$ per hour.
SERIES II.—$k = 0.0055$ per hour.
SERIES III.—$k = 0.0035$ per hour.

Of course the values of the other constants, "K_p" and "K_T" hold only up to the point where it becomes impossible to obtain a value for "*k*."

TABLE I.

Series I—1.3 mols HCOH to 1 mol C_6H_5OH.

Temp. C.	2%.	4%.	6%.	8%.	10%.	K_p.
65°	0.0022[1]	0.00287	0.00373	0.00443	0.00527	0.00039
70	0.00189	0.00336	0.00456	0.00520	0.00606	0.00052
75	0.00270	0.0 461	0.00550	0.00648	0.00711	0.00070[4]
80	0.00300	0.00505	? [3]	?	?	?
85	0.00363	0.00578	?	?	?	?
90	0.00562	0.00765	?	?	?	?
K_T	0.00014	0.00017	0.00019[7]	0.00021[7]	0.00018[7]	?
	Mean value K_T				0.00018	
	Per cent. deviation from mean				5%	

TABLE II.

Series II—2.6 mols HCOH to 1 mol C_6H_5OH.

Temp. C.	2%.	4%.	6%.	8%.	10%.	K_p.
65°	0.00106	0.00164	0.00230	0.00271	0.00345	0.00030
70	0.00126	0.00199	0.00349	0.00392	0.00476	0.00044
75	0.00192	0.00311	0.00436	0.00466	0.00508	0.00061[4]
80	0.00200	0.00342	0.00434	0.00531	0.00564[2]	0.00054[5]
85	0.00297	0.00514	0.00620	?	?	0.00081[4]
90	0.00426	0.00634	0.00729	?	?	0.00076[4]
K_T	0.00012	0.00017	0.00019	0.00019[8]	0.00016[8]	?
	Mean value K_T				0.00016	
	Per cent. deviation from mean				5%	

TABLE III.

Series III—0.65 mols HCOH to 1 mol C_6H_5OH.

Temp. C.	2%.	4%.	6%.	8%.	10%.	K_p.
65°	0.00257	0.00412	0.00447	0.00520[2]	0.00562[2]	0.00060[6]
70	0.00256	0.00483	0.00541	0.00625[2]	0.00663[2]	0.00108[6]
75	0.00425	?	?	?	?	?
80	0.00417	?	?	?	?	?
85	0.00487	?	?	?	?	?
90	0.00574[2]	?	?	?	?	?
K_T	0.00013	?	?	?	?	?
	Mean value K_T					
	Per cent. deviation from mean					

NOTES.—1 Obtained by extrapolation.

2 These values are doubtful; the graphs from which they were obtained are not quite straight lines. They show a slight but distinct curvature indicating a gradual decrease in rate of increasing density.

3 ? These signs indicate that no values were calculable.

4 These values hold for solutions containing up to 6% N NH_4OH.

5 This value holds up to 8% N NH_4OH.

6 These values are doubtful.

7 These hold up to 75° C.

8 These hold up to 85° C.

A possible explanation for the fall in the rate of increasing density is offered in a later paragraph.

For convenience of reference all of the constants found are shown in Tables I, II and III.

Examining the data shown in the tables we note that the most regular results are obtained in series II where there was the greatest excess of formaldehyde, while series III, containing the greatest proportion of phenol, gave hardly any regular values at all. These facts might be explained if we assume that the reaction is one taking place between molecules. The rapid fall of the velocity in the last series might be explained as due to the fact that whatever formaldehyde is present is soon combined with the phenol with the elimination of water. After that the reaction is one of polymerization rather than condensation.[1] It is seen that in series I this decrease in the velocity occurs only in solutions containing 6% or more of the condensing agent and heated at 80° or over. It would appear that beyond those limits the condensation is soon completed, after which the increase in density is due to polymerization. The following experience tends to confirm this supposition. If the mixture is heated at a high temperature, say 110°–120°, for 2–4 hours, water is eliminated so rapidly that it has not sufficient time to evaporate; on cooling, therefore, a water layer is separated. If this is removed and the liquid again heated at 110°–120° C., its density increases but no additional water is separated. From this it would seem that the final resin obtained results from two reactions: 1, condensation with elimination of water and 2, polymerization, no water being eliminated. The point where the first ends and the second begins could not be definitly determined; very likely the second part sets in as soon as some condensation has taken place. In further support of the view that the condensation reaction is between molecules, it was found that the highest densities were obtained in series I, where the main constituents were present in molecular proportions, with formaldehyde enough in excess to make up for loss by evaporation.

A consideration of the regular values in the tables shows that it is possible to represent the specific gravity at room temperature of a given solution of phenol in formaldehyde, containing a known per cent. of ammonia (added as a very dilute solution), after having been heated a given time at a given temperature, by the following equation:

$$s = s_0 + t(k_{p \text{ at T}} + \Delta p \mathrm{K}_{p \text{ at T}'} + \Delta \mathrm{T}\mathrm{K}_{\mathrm{T}}),\ \text{where}$$

s = the required specific gravity or density;

s_0 = the initial density at room temperature;

t = the time of heating;

$k_{p \text{ at T}}$ = The known value of the velocity constant for a given mix-

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[1] Aylesworth patent, U. S., 1,020,593.

ture of formaldehyde and phenol containing "p" per cent. of N NH_4OH by volume and heated at the temperature T;

Δp = the difference between "p" and the per cent. condensing agent in the given solution, $\Delta p = p' - p$;

$K_{p \text{ at } T'}$ = the "per cent. coefficient" of the velocity constant at the given temperature;

ΔT = the difference between T′, the temperature at which the solution is heated and T, $\Delta T = T' - T$; and

K_T = the "temperature coefficient" of the velocity constant.

This equation is offered only as the merest suggestion and can only be used provided we keep within the limits of applicability for each of the constants. Even within these limits it has been found that the deviation of the calculated rise in density from that actually observed is sometimes as high as 10%. As said before, the expression proposed is put forward merely as a possibility.

Summary.

1. An attempt was made to study the velocity of the reaction between formaldehyde and phenol by means of observations of the density at regular intervals.

2. It was found there were two cases, *viz.*, a regular rise in density with the time of heating and a decreasing rate of increase with the time of heating.

3. It was found that the rate of increasing density rises with the temperature and with the per cent. of condensing agent used.

4. It was found that most satisfactorily regular results are obtained when there is greatest excess of formaldehyde.

5. It was found that it is perhaps possible to calculate the rise in density from an equation the applicability of which is very limited.

Before closing the writer wishes to draw attention to the fact that after all, the results given can hardly be taken as valid. Besides it must be remembered that the values are applicable only while the condensation product remains in the liquid state. In view of the extreme crudity of the apparatus and of the many sources of error it would seem advisable that all of these measurements be repeated with an equipment capable of giving more trustworthy results, since the data herewith presented are not nearly as accurate as one naturally desires in scientific investigation. A proper water bath, fitted with a thermostat, and accurate Westphal balances are essential, as are also chemically pure reagents. But although this research has not given any really accurate results, it at least points to the possibility of obtaining valuable data if the work be extended to other catalytic agents, such as sodium hydroxide, sodium bicarbonate sodium carbonate, sodium bisulfate, sodium sulfate, potassium hydroxide, potassium bicarbonate, etc. The writer hopes soon to be in a position to carry forward such an extension of this investigation.

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THE PRECIPITATION OF COLLOIDS BY MEANS OF ALUMINIUM HYDROXIDE.

BY JOHN MARSHALL AND WILLIAM H. WELKER.

Received March 24, 1913.

It has long been common knowledge among chemists that when precipitation of aluminium hydroxide is induced in solutions, or when freshly precipitated aluminium hydroxide is added to solutions containing substances in suspension, and also to liquids containing various substances in solution, these substances are carried down in association with the aluminium hydroxide. Because of this property it is used in industrial chemistry to clarify liquids and to precipitate organic coloring matters. The mordanting property of aluminium salts in the process of dyeing may be attributed to the action of aluminium hydroxide produced in the process.

It also comes into use in mechanical water filters, in sugar analysis and in water analysis as a clarifying and decolorizing agent.

This investigation was undertaken with the view of determining whether aluminium hydroxide had wide application as a precipitating agent in respect to inorganic and organic colloids.

While there are many references in literature respecting the behavior of aluminium hydroxide as a precipitant of various substances, Rohland[1] is the only investigator who apparently has taken up the question of the behavior of aluminium hydroxide as a precipitant of colloids. This investigator, while briefly stating that aluminium hydroxide among other hydroxides precipitates certain colloids, confines his investigations largely to the behavior of clays on colloidal solutions.

The aluminium hydroxide used in our experiments was prepared by precipitating it with dilute ammonium hydroxide from dilute solutions of ammonium alum contained in large glass cylinders. The ammonium hydroxide was slowly added with constant stirring of the solution with a glass rod until finally the liquid yielded a faint odor of ammonia. The precipitate was allowed to subside and was washed several times by decantation with distilled water. It was then collected on a filter and washed several times until the filtrate was fairly free from salts and then transferred to a glass cylinder and again washed by decantation until

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[1] *Z. anorg. Chem.*, **41**, 325 (1904); *Ibid.*, **56**, 46 (1907); *Ibid.*, **60**, 366 (1908); *Ibid.*, **77**, 116 (1912) *Z. Chem. Ind. Kolloid.*, **2**, 177 (1907).