[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MCGILL UNIVERSITY]

MOLECULAR ATTRACTION AND VELOCITY OF REACTIONS AT LOW TEMPERATURES OF UNSATURATED HYDROCARBONS

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The primary purpose of the investigation described in this paper was to attempt to show the effect of molecular attraction on the velocity of a chemical reaction in the absence of a catalyst. The usual way of expressing this mechanism is that a chemical reaction proceeds through intermediate compound formation. To introduce the particular aspect which the authors have in mind mention will be made of a special instance. It was found that acetylene and hydrogen bromide do not form a molecular compound[1] whereas allylene and hydrogen bromide form a definite molecular compound, when these systems are examined by the freezing-point method. It may be deduced from this that hydrogen bromide molecules have a greater attraction for allylene than for acetylene. Acetylene and hydrogen bromide when mixed in the liquid condition, in the absence of a catalyst, were found to be unreactive whereas allylene and hydrogen bromide were found to react slowly even at —80°. On account of the difficulties attached to the preparation of large quantities of pure allylene its reaction with hydrogen bromide was not studied as thoroughly as might be desired and in this investigation ethylene and propylene were used.

The freezing-point curves of ethylene and propylene, with hydrogen bromide as second component, were determined. The tendency for interatomic reaction was investigated and in the case of propylene, where a measurable velocity of reaction was encountered, the products of the reaction were studied.

Freezing-Point Curves

The preparation of the pure hydrocarbons and hydrogen bromide has been previously described.[2] Particular care was taken in the preparation of propylene and it may be of interest to mention that the liquid condensate formed when moist propylene is passed over phosphorus pentoxide was collected. It was examined by the lowering of the freezing point of benzene at three concentrations, 1.35, 2.90, 3.86%, giving molecular weights of 102.6, 102.7, 101.7, respectively. This shows that the condensate is not an alcohol, as the molecular weights would increase with concentration if this were the case. The condensate is probably a polymer of propylene, possibly a trimolecular complex containing some dissolved

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[1] Maass and Russell, (a) THIS JOURNAL, 40, 1561 (1918); (b) 43, 1227 (1921).

[2] Maass and Wright, *ibid.*, 43, 1098 (1921).

propylene. These results are analogous to those obtained with ethylene.[3] Care was taken to ensure the removal of this polymer by a sufficient number of distillations.

The method for obtaining mixtures of known composition of hydrocarbon and hydrogen bromide has been described[4] before. This method enables one to mix the two components in small, sealed glass bulbs. The determination of the freezing points was carried out as previously described. The procedure enables one to mix the two components and measure the freezing point without allowing the constituents to warm up to a higher temperature than a few degrees above the melting point. It was made certain that the freezing point was determined before any chemical action took place. Important portions of the freezing-point curve were found to lie below —160° so that a bath of liquid propylene[3] had to be used in the freezing-point determinations.

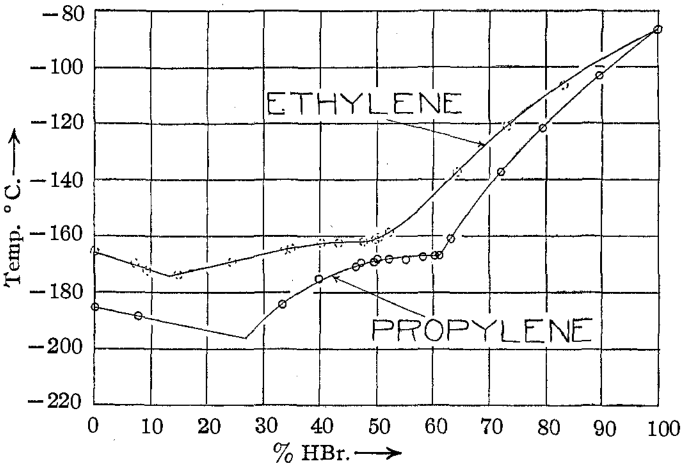

Fig. 1.

The freezing points for the systems ethylene-hydrogen bromide and propylene-hydrogen bromide are plotted in Fig. 1.

The results indicate that the attraction between propylene molecules and hydrogen bromide molecules is greater than that between ethylene molecules and hydrogen bromide molecules. In the first place the form of the propylene curve points to the existence of a molecular compound. In the ethylene curve it is true that there is a slight inflection at the 50% molecular concentration but this is not very pronounced. In the second place, the lowering of the freezing point of hydrogen bromide corresponds to a molecular weight of solute of 42, calculated by making use

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[3] Ref. 2, p. 1099.

[4] Ref. 1 a, p. 1569.

of the cryoscopic constant[5] for hydrogen bromide determined by D. McIntosh.

At 5.9% and 10.0% by weight of propylene the lowering of the freezing point is 16.5° and 29.7°, respectively. This gives molecular-weight values of 36.4 and 33.8, respectively, at these concentrations and hence 42 at infinite dilution. Hence, the propylene was not associated. Ethylene, on the other hand, points to a molecular weight of 47 showing that association of the ethylene molecules takes place when they are dissolved in hydrogen bromide. As has already been pointed out in a previous paper[6] there are three forces of attraction which come into play in a two-component system and in this case the above facts show that the force of attraction between ethylene and hydrogen bromide is small. For details of the argument reference may be made to the above-mentioned paper.

Velocity of Chemical Reactions

What has gone before shows that ethylene and propylene correspond to acetylene and allylene, respectively, although the difference in attraction for hydrogen bromide of the former two is not quite so pronounced as that of the latter. The relative tendency towards the interatomic reaction of ethylene and propylene for hydrogen bromide was therefore made the subject of a careful study.

A few preliminary experiments showed that what was anticipated occurred. Ethylene and hydrogen bromide when mixed in the liquid state did not react, whereas propylene and hydrogen bromide reacted quickly at room temperature and relatively slowly at —78°. It was soon found that the latter reaction presented several points of interest and a method was therefore devised to measure and study the velocity of the reaction and at the same time to prove as definitely as possible that the difference in reactivity was not due to a catalyst present in the propylene and absent from the ethylene.

The propylene and hydrogen bromide were mixed in 1:1 molecular proportion by means of the same apparatus that was used in the freezing-point experiments. This insured that the two were mixed and sealed in glass bulbs without the possibility of moisture entering the mixture and at the temperature of liquid air where no reaction takes place. Small glass bulbs which had been cleaned by chromic acid solution and thoroughly dried were used. Sufficient propylene and hydrogen bromide were condensed by use of liquid air to fill the bulb almost full of liquid when warmed to the temperature at which the experiment was to be carried out. The bulbs were then placed in a constant-temperature bath and at various noted times they were transferred back into liquid

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[5] McIntosh and Reid, THIS JOURNAL, **38**, 615 (1916).

[6] Maass, Boomer and Morrison, *ibid.*, **45**, 1437 (1923).

air and kept there until the contents were to be analyzed. The velocity of the reaction was measured at two temperatures, —78.2° and 0°, carbon dioxide-ether mixture and an ice water-bath being employed as thermostatic media.

To analyze the contents of a bulb the latter was taken out of the liquid air, the wire attached to it quickly removed, the tip broken off and the bulb dropped into a liter suction flask partly filled with water, a rubber stopper being quickly inserted at the moment of the dropping of the bulb. The suction flask was connected to two wash bottles partly filled with water. It was possible in this way to dissolve any uncombined hydrogen bromide, the uncombined propylene passing off through the wash bottles. The bulb remained at a temperature where the vapor pressure of the contents was negligible until the bulb reached the water. The whole apparatus was then well shaken until the last trace of the white fumes of hydrobromic acid had dissolved in the water. The contents of the wash bottles were then poured into the suction flask and the walls thoroughly rinsed with distilled water. Amounts of oil varying with the lengths of time that the bulb had been left in the temperature bath separated as globules in the flask.

The next procedure was the determination of hydrobromic acid. A standard alkali solution was first used with phenolphthalein as indicator. Since the alkali acted slowly on the oil the end-point was not sharp and so the following method of analysis was developed.

Five cc. of a 10% ferric alum solution together with a few tenths of a cc. of 0.1 *N* ammonium thiocyanate solution (sufficient to give a pink coloration) was added and then the whole titrated to the discharge of the color with 0.1 *N* silver nitrate solution. The latter combined first with the hydrobromic acid and then with the thiocyanate so that the oil (consisting mainly of *iso*propyl bromide) was not attacked and a distinct end-point was obtained. This method can be used for hydrobromic acid but not for hydrochloric acid, since the solubility product of silver thiocyanate is less than that of silver chloride but greater than that of silver bromide.

The following is a sample calculation of the amount of hydrogen bromide combined with propylene as determined by the method of analysis.

The bulb remained in the bath of carbon dioxide and ether for 141 hours; there were present at the start 0.004310 mole of hydrogen bromide and 0.004305 mole of propylene; 14.60 cc. of 0.1 *N* silver nitrate solution was required for titration, 0.53 cc. being required for the added ammonium thiocyanate. Therefore 14.07 cc. of 0.1 *N* silver nitrate solution was required for the hydrobromic acid, equivalent to 0.001407 mole of hydrobromic acid. Since this corresponds to the amount of hydrogen bromide left uncombined, the percentage of hydrogen bromide which had combined in 141 hours was $\frac{0.004310 - 0.001407}{0.004310} \times 100\% = 67.4\%$.

A blank experiment showed that no measurable combination between uncombined propylene and hydrogen bromide occurred after the bulb had been broken. The percentages are probably accurate to at least 1%.

These percentages of combined hydrogen bromide plotted against time are shown graphically in Fig. 2. Curves A and B represent the same points, A being plotted on a much larger scale and its continuity shows the accuracy with which experiments could be reproduced independently of the fact that propylene and hydrogen bromide were prepared fresh at various times. All the mixtures were practically of equimolecular proportions with a variation of but a few tenths of 1%. It is worth mentioning at this point that ethylene and hydrogen bromide kept in bulbs for several days at —78.2°, when analyzed in the manner described above were found to be unchanged.

It will be noticed from Curve A or B of Fig. 2 that the velocity of the reaction is constant at the start, approximately 0.083% of hydrogen bromide combining per minute. The rate decreases and after 200 hours practically no further reaction apparently takes place. A number of bulbs were kept for two weeks at —78° and on analysis confirmed this, 71% being the maximum amount combined. This was a most unexpected result, as the original mixtures contained sufficient propylene to combine with all the hydrogen bromide if propyl bromide is the only product of the reaction. The explanation for this apparent anomaly will be considered later.

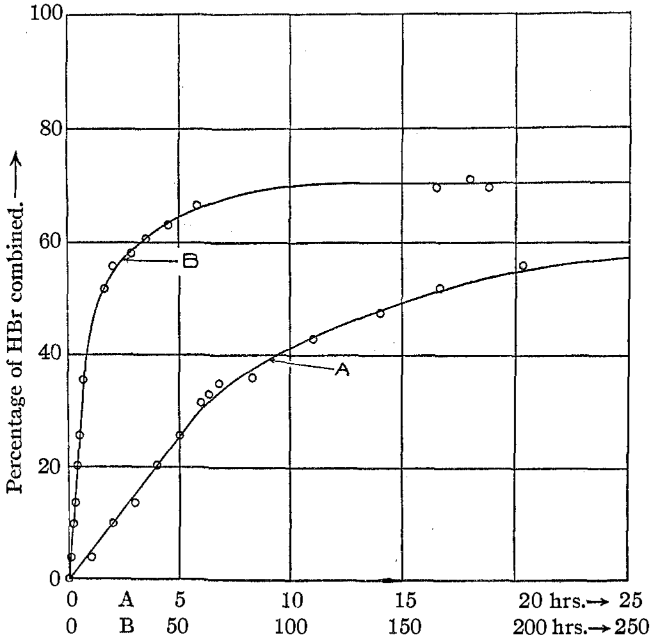

Fig. 2.

The reaction was found to be catalyzed by an excess of hydrogen bromide. This was proved by varying the ratio of the initial concentration of the reactants, the percentage of hydrogen bromide combined being calculated on the basis of the maximum amount that could combine to form a propyl bromide. A few results are as follows.

Mol. % of HBr in bulb at start	20.0	35.0	50.0	65.0
Time in bath, hours	49	47	47	47
HBr combined, %	2.3	14.5	64.0	84.0

The velocity of the reaction between propylene and hydrogen bromide was also measured at 0°. Thick-walled glass bulbs were used so that the bulbs and contents could be transferred directly from liquid air into the ice-bath and plunged back into the liquid air, without breaking, when the reaction was to be stopped. The results obtained at this temperature are shown graphically in Fig. 3, Curves A and **B** representing the same points on two different scales.

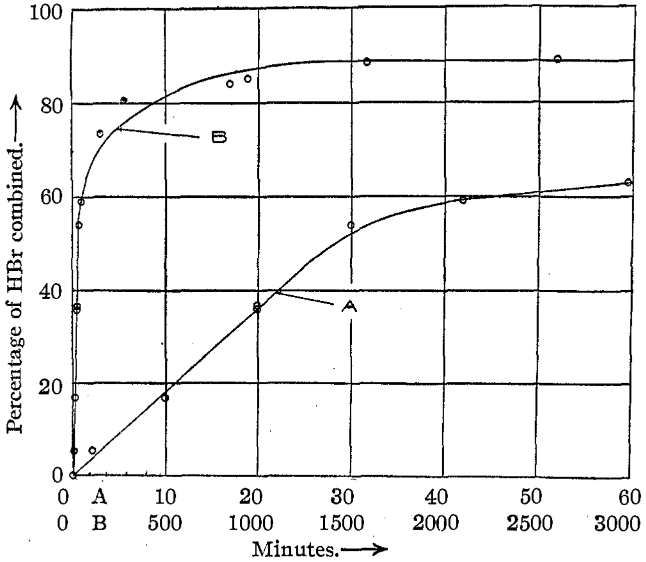

Fig. 3.

It is seen that the velocity of the reaction is again constant at the start, 1.7% of hydrogen bromide combining per minute, this being twenty times as fast as at —78.2°. Here again the velocity of the reaction decreases and becomes zero after about 24 hours. The final amount combined, about 89%, is higher than that combined at the lower temperature and again a definite maximum is reached. Experiment showed that the small amount of gaseous phase above the liquid did not vary sufficiently in volume from bulb to bulb to affect the results. Agitation while in the bath had no effect on the velocity of the reaction.

A bulb containing a 1:1 molecular mixture of liquid ethylene and hydrogen bromide was placed in an ice-bath and kept there for several days. Subsequent analysis showed that no measurable reaction had taken place, although propylene under the same conditions would have reacted to what will later be seen to be completion. To make certain that the difference in reactivity was not due to a catalyst present in the propylene and absent from the ethylene, bulbs were prepared containing molecular percentages 25:25:50 of ethylene, propylene and hydrogen bromide, respectively, and placed in the two temperature baths mentioned above. These bulbs contained sufficient hydrogen bromide to react with both propylene and ethylene. Nevertheless, the amount of hydrogen bromide combined corresponded solely to the amount of propylene which would have combined as calculated from the velocity curve of propylene and hydrogen bromide. That is, less than half the hydrogen bromide was combined after an adequate time in the temperature baths.

The interpretation advanced to explain the relative reactivity of propylene and ethylene is that the molecular attraction of propylene for hydrogen bromide as indicated by freezing-point measurements is greater than that of ethylene for hydrogen bromide. Molecular attraction tends to keep molecules together for a sufficient length of time to allow interatomic changes to take place. Violent collision may be required in order to cause the atomic vibrations in a molecule necessary for the reaction but this must be followed by the continued close proximity of the two reacting molecules. The attraction between propylene and hydrogen bromide molecules as such is sufficiently great to cause a large number of pairs to be available for such a process. It follows that the velocity of the reaction between propylene and hydrogen bromide will be much greater than that between ethylene and hydrogen bromide where the molecular attraction is much less. A catalyst can supply the lack of sufficient attraction between ethylene and hydrogen bromide and so enable them to combine.

Products of the Reaction between Propylene and Hydrogen Bromide

Quite apart from the above results which are the outcome of the main object of this investigation, there remains a consideration of the reaction between propylene and hydrogen bromide in which an explanation must be given for the apparent stopping of the reaction before all of the hydrogen bromide has combined.

It was first of all shown that the end concentration reached was not the result of an equilibrium.

Several bulbs were kept at a temperature of —78.2° for a week when, according to the velocity of reaction at this temperature, 70% of the hydrogen bromide should have combined. The bulbs were then placed in an ice water-bath for a day where if the end-point were a question of equilibrium 89% should have combined. Analysis showed that they had reacted to 69% which corresponds to what might be expected from the first temperature bath, that is, no further reaction had taken place and therefore there was no reversible equilibrium.

The only explanation left is that, apart from the main reaction, which is, the formation of a propyl bromide, a side reaction takes place. Such a side reaction may consist in the formation of a polymer of propylene, this reaction being catalyzed by the hydrogen bromide,

$$n(CH_3-CH=CH_2) \xrightarrow{HBr} (CH_3-CH=CH_2)_n \qquad (1)$$

or a reaction between two molecules of propylene with one of hydrogen bromide

$$2CH_3-CH=CH_2 + HBr = C_6H_{13}Br \qquad (2)$$

Either of the reactions, 1 or 2, would explain the presence of uncombined hydrogen bromide at the end of the reaction in a 1:1 mixture.

Evidence in favor of such a side reaction was given by the fact that the analysis of bulbs which had been kept in either of the temperature baths for an adequate length of time showed the absence of propylene in spite of the uncombined hydrogen bromide.

In order to investigate the side reaction further, a large quantity of a 1:1 mixture of propylene and hydrogen bromide was prepared, some 100 cc. of liquid being obtained. This was kept at —78.3° for a week, at the end of which time it will be seen by reference to Fig. 2 that the reaction had gone to completion.

The tube containing the mixture was connected through a stopcock with a glass apparatus consisting of other tubes fitted with stopcocks and attached to a vacuum pump and manometer so that the mixture could be fractionated. The first part of the fractionation was carried out at 0°, the condensation being accomplished by a bath of carbon dioxide and ether. The first two-thirds of the mixture was distilled slowly while the liquid was frequently shaken; it contained practically all of the uncombined hydrogen bromide. One half of the remainder was condensed in a separate tube. It will be called Fraction A and the residue Fraction B. Fraction A, consisting of about 10 cc. of liquid and registering a vapor pressure of 6.8 cm. of mercury at 0°, was subjected to a separate series of fractionations. Three final fractions were obtained, the middle fraction consisting of the largest portion registered a pressure of 6.75 cm. of mercury at 0°. The more volatile fraction registered a slightly higher pressure due to the presence of a small amount of hydrogen bromide. The residue registered a lower vapor pressure which decreased continuously as more and more of it was distilled. The vapor pressure of the middle portion corresponds to that of *iso*propyl bromide, the value given in the literature at 0° being 6.9, as compared to 4.16 cm. for the vapor pressure of the *normal* propyl bromide. The molecular weight of the middle portion was determined by the Victor Meyer method, the three values obtained being 127, 129 and 129 as compared with 123, which is the calculated molecular weight for a propyl bromide.

The somewhat higher value for the molecular weight obtained points to the presence of a compound of higher molecular weight in the *iso*propyl bromide. Since this would be largely contained in the residue called B which was left from the first distillation of the whole mixture, this residue consisting of 10 cc. of liquid was gradually distilled. The pressure of the residue was measured each time after the removal of a small portion by distillation and eventually reached a constant value of 0.5 cm. of mercury at 22°. This last portion was then subjected to molecular-weight determinations and analyzed for bromine content.

In order to prevent loss of material in handling, a small, fragile glass bulb was blown at the end of a tube the other end of which consisted of a ground-glass joint fitting to the distillation apparatus. The ground-glass joint and bulb were weighed, connected to the apparatus, evacuated, the stopcock leading to the oil was opened and an adequate amount of the oil distilled into the bulb. The bulb was sealed off, the ground-glass joint detached, cleaned from lubricating grease and the weight of the oil in the bulb accurately obtained. The molecular weight of the oil was determined by the lowering of the freezing point of benzene. The following were the molecular weights obtained with corresponding concentrations of benzene solutions; 165.1 at 1.21%; 164.4 at 2.23%; 165.7 at 3.61%. The calculated molecular weight of hexyl bromide is 165 agreeing very closely with the value found.

Two determinations[7] of the bromine in the oil were made. The values found were 42.9% and 45.1%. The calculated percentage of bromine in hexyl bromide is 48.5%, agreeing within what the authors believe to be their experimental error in the bromine analysis.

The boiling point of the oil was approximately measured by a method described by Smith and Menzies.[8] Condensation of the liquid in the upper portion of the tube was found to start at 142°, vigorous boiling taking place at a few degrees higher. Normal bromohexane has a boiling point of 156°; both 2-bromohexane and 1-bromo-2-methylpentane have boiling points lying between 142° and 145°. A consideration of the possible isomers of bromohexane which could form from propylene and hydrogen bromide shows that there are only four, namely, 2-bromohexane, 1-bromo-2-methylpentane, 2-bromo-4-methylpentane and 1-bromo-2,3-dimethylbutane. The normal bromohexane cannot be formed in this particular reaction. The boiling point experimentally found is, therefore, in agreement with those of isomers of bromohexane which might be formed.

The results enumerated above seem to point to the fact that *iso*propyl bromide is the main product of the reaction between propylene and hydrogen bromide. A side reaction takes place involving the formation of a hexyl bromide. The velocity of the main reaction increases with rise in temperature to a far greater extent than the velocity of the side reaction. This explains why at —78.2° the percentage of uncombined hydrogen bromide at the end of the reaction is less than at 0°.

The reaction between hydrogen bromide and propylene lends itself to a study of the temperature coefficient of the velocity of a reaction at low temperatures. This, together with the catalytic effect of hydrogen bromide which seems to influence only the main reaction, needs further investigation. Similar reactions between propylene and hydrogen chloride are also being studied at the present time. To obtain a theoretical equation representing the velocity of the above reactions involves a number of complicating factors. For one thing, there is a considerable change in density during the course of the reaction and this has to be evaluated before any attempt in this direction can be made.

Acknowledgment is hereby made of the assistance of a Ramsay Memorial Fellowship, a part of the time of which made possible the completion of this investigation.

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[7] Dains, Vaughan and Janney, THIS JOURNAL, **40**, 936 (1918).

[8] Smith and Menzies, *ibid.*, **32**, 897 (1910).

Summary

The freezing-point curves of ethylene and propylene with hydrogen bromide as second component were determined. The results indicate that propylene molecules have a greater attraction for hydrogen bromide than have ethylene molecules.

It was shown that hydrogen bromide and propylene react chemically with each other whereas in the case of ethylene there is no reaction.

It was shown that this difference between the propylene and ethylene was not due to a catalyst. The ideas advanced, that the velocity of a chemical reaction may be dependent on the attraction between the reacting molecules, account for this difference.

The velocity-of-reaction curve of propylene and hydrogen bromide was determined at —78.2° and at 0°. The main product of the reaction was found to be *iso*propyl bromide. It was also shown that a side reaction involving the formation of a hexyl bromide took place.

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

DENSITY AND HYDRATION IN GELATIN SOLS AND GELS

BY THE SVEDBERG

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Some time ago Svedberg and Stein communicated a series of measurements on the density of gelatin sols made with the object of obtaining information regarding the hydration of gelatin.[1] As pointed out by F. E. Brown[2] these measurements are insufficient for the purpose in question because the density values were not corrected for the difference in density between the gelatin and the solutions studied. Instead of trying to correct the data given in the paper by Svedberg and Stein it was found easier and also more rational to measure directly by means of a volumetric method the volume change which occurs when gelatin is dissolved in a liquid. The results thus obtained showed that it would be interesting to determine also by means of the same method the volume change occurring in the swelling of gelatin, that is, in the formation of a gelatin gel. A few experiments of this kind also have therefore been carried out.

The determinations were made in the following way. Gelatin leaves were kept in a moist atmosphere for a few hours to make them flexible and from them strips of about 35 mm. broad were cut. Such strips were rolled into cylinders of about 20 mm. diameter and containing about 1 g. of gelatin. These gelatin rolls were dried over sulfuric acid and

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[1] Svedberg and Stein, THIS JOURNAL, **45**, 2513 (1923).

[2] Brown, *ibid.*, **46**, 1207 (1924).