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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DENSITY AND HYDRATION IN GELATIN SOLS AND GELS

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RECEIVED JULY 17, 1924 PUBLISHED DECEMBER 13, 1924

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

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

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

then heated for some hours at 100–105°. Immediately before a determination a gelatin roll was weighed and by subtraction or addition of a little dry gelatin was made to weigh exactly 1.000 g. It was then introduced into the dilatometer (Fig. 1).

This consists of a cylindrical vessel A with a ground-in stopper carrying a capillary C of about 1 sq. mm. section and a side tube B. The gelatin roll E rested on a platinum disk D fixed to a glass rod which is suspended on a 0.1-mm. platinum wire. This wire passes through the glass capillary of the dilatometer and can be fixed in the proper position by means of rubber rings around the capillary. After the gelatin roll has been fixed in the upper part of the dilatometer vessel the latter is filled with liquid paraffin, the stopcock F is closed and the dilatometer is evacuated from the capillary side by means of an aspirator in order to remove air bubbles. By successive evacuation and introduction of air this can be done in a few minutes. The proper amount of solvent is then introduced through the side tube. Rubber strings are put around the stopcock and others are passed around the stopper with the capillary to the side tube B. These precautions are necessary to keep the volume of the dilatometer perfectly defined. The apparatus is then placed in a thermostat and allowed to reach constant temperature. After an hour the stopcock F is closed and the level of the paraffin in the capillary C observed. When this has become constant the gelatin roll E is lowered into the solvent layer and the movement of the paraffin in the capillary observed. After it has again become constant the support for the now dissolved gelatin is raised to the same level that it had at the beginning of the experiment in order to have the same length and, accordingly, the same volume of platinum wire in the dilatometer at the end as at the beginning of the determination. If the exact value of the cross section of the capillary is known the volume change may be found by multiplying the cross section by the number of millimeters' distance over which the paraffin in the capillary has moved.

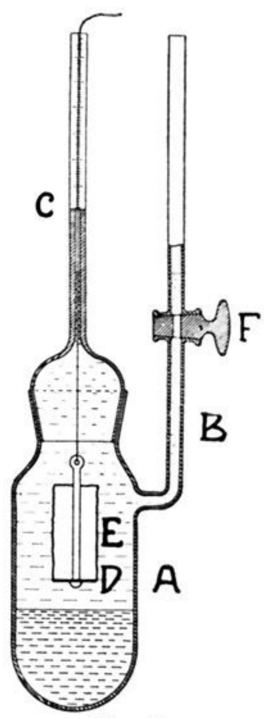


Fig. 1.

Some preliminary tests showed that the content of water in the gelatin used had a great influence upon the values obtained. In all cases a contraction was observed but the contraction was much greater when dry gelatin was used. Three kinds of gelatin were tested: two samples of ordinary "soft" food gelatin and a sample of "hard" gelatin for photographic purposes. All gave practically the same values if heated for a few hours at 100–105°. One of the samples of food gelatin gave lower values when not heated but only dried over sulfuric acid.

The determinations of Tables I to IV were made at 35.2°. Table I and Fig. 2 give the data for the influence of water in the gelatin.

Table I

Influence of Water in Gelatin upon Contraction

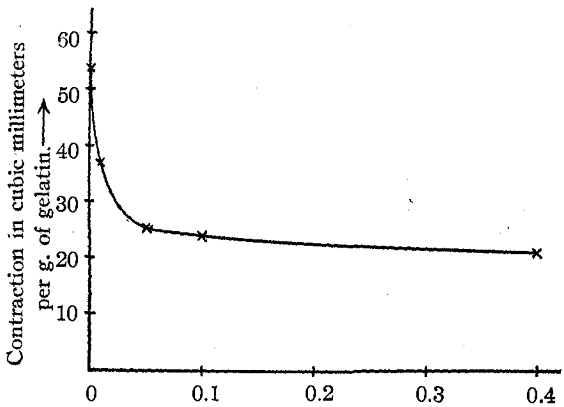
G. of water per g. of gelatin	0	0.02	0.05	0.1	0.4
Contraction, cubic mm. per g. of gel. in 100 cc. of H_2O	54	37	25	24	21

The contraction was found to be independent of the volume of the solvent as shown by the data given in Table II.

Table II

Effect of Volume of Solvent upon Contraction

Water, cc.	100	50	25
Contr., cubic mm. per g. of gelatin	54	57	53



→ G. of H_2O per g. of gelatin.
Fig. 2.

Strong acids and alkalies diminish the contraction considerably as shown by Table III and Fig. 3.

The action of sodium hydroxide could not be studied at higher concentrations because of the chemical action of the alkali on the gelatin.

Weak acids and alkalies, neutral salts and non-electrolytes have no appreciable effect on the contraction, as shown by Table IV.

The value of the contraction was also measured at different temperatures down into the region where no sol formation but only swelling of the gelatin to a jelly takes place. In Table V some of these determinations are given.

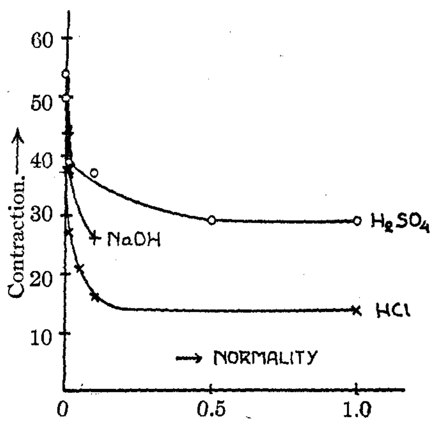


Fig. 3.—Contraction in cubic millimeters per g. of gelatin.

The contraction increases with decreasing temperature, but there seems to be no discontinuity when passing over from the region of sol formation to the region of gel formation. Experiments at lower temperatures gave still higher values for the contraction, but the process of swelling required several days at temperatures lower than 25°, which caused uncertainty in the values obtained.

Table III

Contraction Induced by Acids and Alkalies

In cubic mm. per g. of gelatin, dissolved in 100 cc. of solvent

Normality N	Contraction in HCl	Contraction in H_2SO_4	Contraction in NaOH
0.0	54	54	54
0.001	38	50	..
.01	27	39	44
.05	21	..	..
.1	16	37	26
.5	..	29	..
1.0	14	29	..

Table IV

Effect of Weak Acids and Alkalies, Neutral Salts and Non-Electrolytes on Contraction

The volume used was 50 cc. Contraction in terms of cubic mm. per g. of gelatin

Solvent	CH_3COOH	NH_3	KCl[a]	K_2SO_4	KCNS	Urea	Sucrose
Normality, N	0.1	0.5	0.1	0.1	0.1	0.1	0.1
Contraction	53	55	54	53	54	56	54

[a] 100 cc. used.

Table V

Contraction at Different Temperatures when Gelatin Is Brought in Contact with 50 Cc. of Water

Temp., °C.	48.2	41.3	35.2	30.2
Contraction, cubic mm. per g.	42	50	54	59
	sol	sol	sol	gel

Analogous determinations for other proteins are planned. A detailed discussion of the results will be postponed until more data are collected.

Summary

1. The volume change which takes place when gelatin is brought into contact with water has been measured by means of a direct volumetric method. The reaction is always accompanied by a contraction.

2. The contraction observed decreases with increasing content of moisture in the gelatin. For dry gelatin it is about 54 cubic millimeters per gram of gelatin dissolved in water at 35°.

3. Strong acids and alkalies diminish the contraction considerably. The first traces of acid or alkali added have the relatively strongest action.

4. Weak acids and alkalies as well as neutral salts and non-electrolytes do not influence the contraction markedly.

5. The contraction increases with falling temperature. No discontinuity is observed when the temperature passes into the region of gel formation.

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