ON THE FREEZING OF GEL.

By Kyoji KINOSHITA.

Received June 18, 1930. Published September 28, 1930.

The structure of gels which are formed by setting of the hydrophilic colloids such as gelatine, agar or starch etc. have been studied by numerous authors, and several opinions[1] were given on this subject. Formerly it was considered to be a homogeneous or one phase system. But now, generally, two phases theory is adopted for, in some cases, even optical resolution into two phases are possible. The two phases theory are subdivided into two, namely liquid-liquid system and solid-liquid system. Whichever we may take, it will be interesting to study the nature of water in the gel. The present experiment have been undertaken to study this problem by freezing of gels.

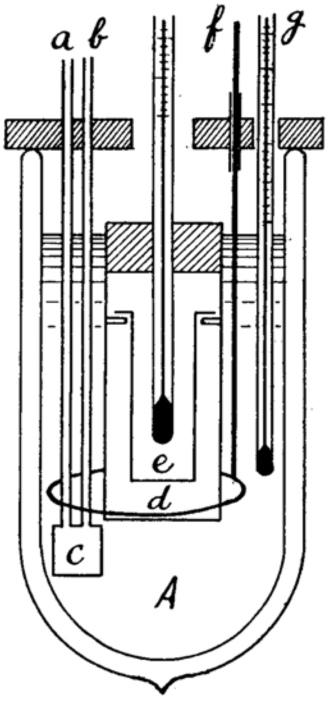

Fig. 1.

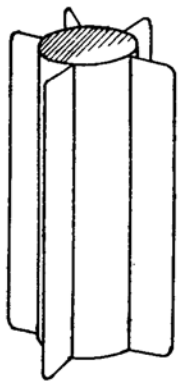

Fig. 2.

(1) For example, Hardy, *Proc. Roy. Soc.*, A, **66** (1900), 95; Lloyd, *Biochem. J.*, **14** (1920), 147, 584; Bogue, *J. Am. Chem. Soc.*, **44** (1922), 1343.

Moran[1] and Hardy[2] observed the microstructure of gels and the volume change by freezing. Most interesting result drawn from their experiments is an equilibrium relation between gel and ice.

According to Moran, when 12–40% gelatine gel was cooled at –3°C a part of water separated from the gel and solidified into ice and covered the unfrozen gel. Taking off the shell of ice the internal gel has a constant concentration depending on the freezing temperature. For example, the gel frozen at –3°C. always has 54.3% internal gel concentration and at –19°C. internal gel concentration reached 65.2%. He also reported that the frozen gel reabsorbs water if it was warmed and the gel comes back to its initial concentration. From these and other observations he concluded that there are two kinds of water in a gel, namely the water combined with gelatine particles and the water contained in a capillary formed by the aggromeration of these particles. In the case of gelatine gel 30% of water is said to combine with gelatine particles.

Experimental. Commercial food gelatine was used all through the experiments, ash content of which was found to be 0.5%.

Cooling apparatus used for the freezing of gel is shown in Fig. 1. *A* is a Dewar's vessel of about 1 litre capacity and is filled with petroleum ether. The liquid air was dropped into the copper vessel *c* through the tube *a*, which then vaporizes and escapes through another tube *b*. *d* is a vessel made of thin copper plate and contains a small copper vessel *e* of about 20 c.c. capacity. The vessel *e* contains gelatine gel, and a Beckmann's thermometer is inserted into the gel. *f* is a stirrer, and *g* a pentane normal thermometer for the measurement of the bath temperature.

Gelatine, stored in a desiccator, is weighed and some amount of distilled water is added. After the swelling of gelatine was completed it is heated on a water bath for a while to obtain a homogeneous solution. A part of the solution is transferred into the vessel *e* and let to set into a gel. Remaining portion is taken into a porcelain crucible and is heated to dryness at 100°C. in an air bath untill the weight constant is attained. The concentration of the gel is determined by this manner.

Beckmann's thermometer is inserted into the gel contained in *e* and the reading is taken every 30 seconds in order to construct a cooling curve of the gel. The Beckmann's thermometer, however, is not sufficiently sensitive to the small change of temperature, so the bulb of thermometer is dipped into mercury contained in a copper cylinder to which some copper

(1) Moran, *Proc. Roy. Soc.*, A, **112** (1926), 30.
(2) Hardy, *Kolloid-Z.*, **46** (1928), 270.

wings are attached (Fig. 2). This small cylinder with wings is inserted into gel and the temperature of gel is measured indirectly. Gelatine gel increases its volume when it is frozen, and we have experienced that, if we insert a thermometer directly into a gel the mercury bulb is subjected to a high pressure, so that not only the thermometer indicates an incorrect reading but also it is liable to be broken by the pressure. Using the above described small cylinder we can get rid of these inconveniences.

Results of Measurement. Some of the cooling curves of gels, which we have obtained in the various concentrations of gelatine (from 5% to 60%) are shown in Fig. 3. As seen from the figure, the phenomena of supercooling is appeared very markedly. This may explain as a result of protective actions of gelatine on the formation of ice nucleus and on the growing of ice crystals.

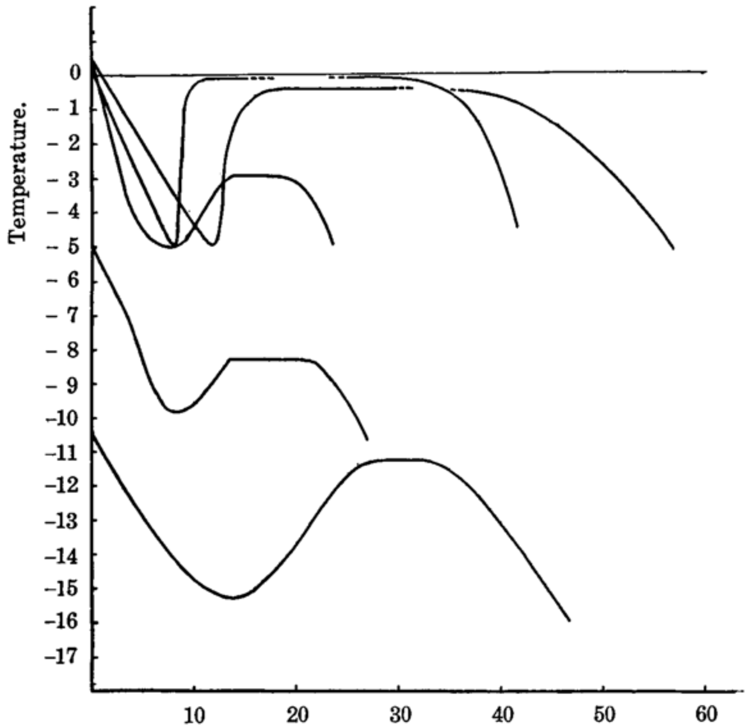

Fig. 3.

It is noteworthy, moreover, that the structure of the frozen gel thus produced differ from each other according to their concentrations. Namely, in the case of gel below 15% frozen in a cylindrical vessel, the concentric thin layers of ice and gel are seen. The layers come alternately and the thickness of which are about 0.5 mm. Of these alternating shells the first shell is always of ice. When it is left to thaw, then again it absorbs water from ice into the layer of gel. However, a little quantity of water can be squeezed out by pressing, immediately after it thawed. Therefore, it seems that the melted ice is reabsobed by the swelling of the gel if we do not press it.

Formation of these shells can be explained in the following manner. At first water which can be separated by cooling comes out of gel (dehydration of gel is caused) and forms shell of ice but the effect of this dehydration of gel does not go very deep into the gel owing to its poor heat conductivity. Thus the thin gel layer under the shell of ice is concentrated by dehydration, and this layer of gel does not freeze by cooling, for its freezing point is lowered by dehydration so that it remains unchanged. Then the cooling effect goes deeper and again a layer of ice is formed. This process is repeated and thus the alternate shells of ice and gel are produced.

Frozen gel of stronger than 20% shows somewhat different structure from that of weaker than 15%. In this case it is a very hard mass of pale brownish white colour and the separation of water as ice cannot be observed with eyes. By the use of a microscope small ice crystals can be seen here and there.

The gelatine gel increases its volume by freezing. Moran measured the change of volume by using a dilatometer, but I could not do any quantitative measurement on this point.

Similar cooling curve can be seen in a case of starch gel. The frozen starch gel is white in colour, and when it is left on the funnel to thaw it secredes water in drops. Agar gel slso becomes whitish and are found many cracks. The frozen agar gel, when left on a funnel to thaw, it separates water drop by drop, and we can press out considerable amount of water from it.

Conc. of gelatine gel by weight %.	Freezing temeprature °C.
5	− 0.10
10	− 0.42
15	− 2.96
20	− 5.66
25	− 8.33
30	− 9.74
40	−11.25
60	−12.65

It is almost a doubtless fact that the hydrophilic colloids are in hydrated states. Many authors have reported the investigations on the degree of hydration. Moran determined the quantity of water separated from a frozen gel as ice, and concluded that the degree of hydration in the case of gelatine is about 30%.

The freezing temperatures of various gels obtained by the present experiment are shown in the table above.

Plotting these values on a temperature concentration diagram we obtain a curve of inverse S type (Fig. 4). In the case of 5% and 10% gel we find that its freezing temperature is nearly equal to, or little lower than that of pure water. The form of cóoling curve obtained in this case is similar to the curve which can be obtained when the pure ice is separated from the solution. In the case of 15–30% gel freezing temperature falls suddenly, and in the 40% up to 60% gel freezing temperature curve becomes asymptotical to the axis of concentration.

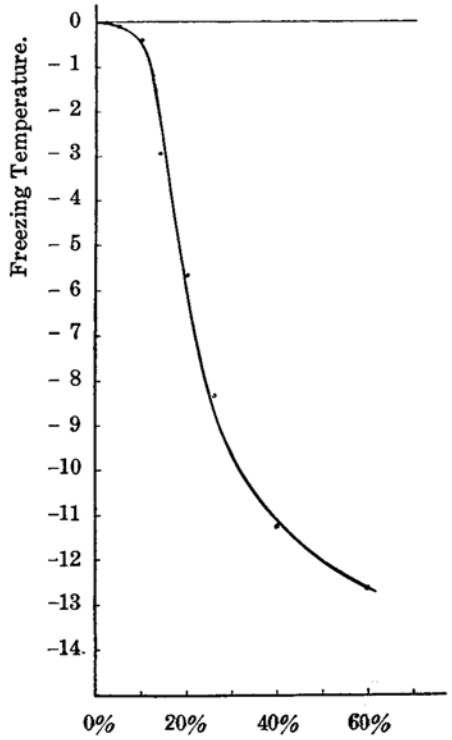

Fig. 4.

Now let us assume that the gelatine particle can take any degree of hydration according to its concentration. These hydrated water molecules have their own strength of hydration, some of them may cling to the particle very strongly and others may be very weakly attach to the particle, just as we can see in the case of ion-atmosphere around the ion of strong electrolyte. Weakly attached water must be separated when gel is subjected to dehydration, and the constitution of dehydrated gel must depend on the process and intensity of dehydration. In the above experiments 5–15% gel has a weakly combined water which can be separated out by freezing, so that there remains the mixture of gel and ice. In the gel more concentrated than 15% there is no water which can be separated by freezing, and hence it freezes in a hydrated state, and is turned into a pale brownish white mass. In the case of 40–60% gel, the freezing point curve runs asymptotically to the axis of concentration. From this fact it is probable that some water must be combined in gel rather strong, in the form of chemical compound or of solid solution. By these assumptions we can explain the above described formation of alternating shell of ice and gel.

In conclusion, I should like to express my hearty thanks to Prof. J. Sameshima for his kind guidance throughout my experiments.

Chemical Institute, Faculty of Science,
Tokyo Imperial University.