The Gel-Elasticity of High Polymers

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The elasticities of the reversible gels of various high polymeric substances at ordinary concentrations and room temperatures are concluded to be essentially rubber-like on the basis of experiments about (1) the dependence of the gel-elasticity coefficient on temperature, (2) the dependence of the second order transition point of the gel on the concentration, (3) the dependence of the gel-elasticity coefficient on the concentration and (4) the detection of Gough-Joule effect of the gel.

The dependence of the gel-elasticity on the concentration and the molecular weight of high polymer is discussed theoretically from the viewpoint of rubber-like elasticity of the gel.

INTRODUCTION

The term gel has been very loosely used by many authors, but here a gel is defined as a colloidal disperse system with the properties of a solid, while a sol is the same system with the properties of a liquid. The rigidity, namely gel-elasticity is one of the most remarkable properties which distinguish gels from sols. Some gels are liquefied to sols on heating but again they can be solidified on cooling. Such are called reversible gels. Many natural high polymeric substances such as agar, gelatin and starch form reversible gels. For many years, colloid chemists have turned their attention to the gel-elasticity and several works were conducted from the viewpoint of colloid chemistry.[1][2][3][4]

Recently J. D. Ferry[5][6] for gelatin and T. Nakagawa[7] for agar measured the gel-elasticities with a great accuracy and obtained some valuable information about their properties. Nakagawa deviced a sensitive method to measure the gel-elasticity and verified the existence of very slight but distinct rigidity in even an extremely dilute aqueous solution of agar which has been usually considered to be a sol.

Up to the present, many investigators, with a few exceptions[5], considered that the gel-elasticities were energetic like crystal lattice[7][8] or a rigid framework.[9][10][11][12] Indeed, the elasticities of some kinds of gels may be energetic, but it can not be concluded that it is true for all kinds of gels. It is desirable to study as many kinds of gels as possible.

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The present author studied the gel-elasticity in various ways and with large variety of gels, especially of natural high polymeric substances and their derivatives. After those investigations, he has come to a conclusion that the elasticities of these reversible gels of high polymer are essentially rubber-like at ordinary concentration and room temperature.

In this comprehensive report, it will be discussed why the author came to the above conclusion. The elasticities were measured by Schwedoff-Hatschek-Poole's concentric cylinder method[7][30] for dilute gels and by Ewing's bending method[31][40] for concentrated gels.

I. THE TEMPERATURE DEPENDENCE OF THE GEL-ELASTICITY

As has been well known, there are two types of elasticity. One is the energy elasticity whose typical example is crystals. The other is the entropy elasticity, and the elastic rubber is its typical example. It has been derived thermodynamically[8][13] that the elasticity is energy type or entropy one according as it decreases or increases with temperature.

Under some experimental conditions, the temperature dependencies of the elasticities of the hydrogels of agar and gelatin were observed as shown in Figs. 1 and 2. They decrease with increasing temperature in the same manner as already reported by previous investigators.[4][5][8][12][14] Therefore, these elasticities have been concluded to be energetic as mentioned above.
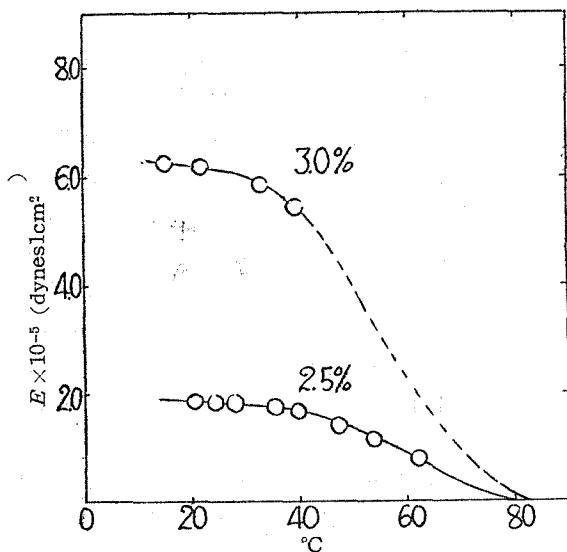

Fig. 1.
Temperature dependence of elasticity
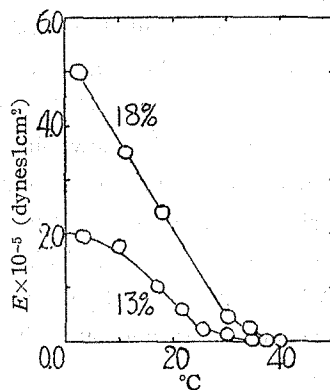coefficient of agar-H_2O gel.

Fig. 2.
Temperature dependence of
elasticity coefficient of
gelatin-H_2O gel.

The present author studied the temperature dependencies of many other reversible gels over wider range of the temperature and it was found that the elas-

ticities of these gels decrease with temperature abruptly at high and low temperature regions, but at room temperature region, they increase in many cases. Therefore, the temperature dependency of the elasitcity of reversible gel may be expressed typically by such a form as is shwon in Fig. 3, which is the case of 16 % polyvinyl alcohol ($\bar{P}$ = 1680) in 85 % glycerol[36]. In this typical case, the elasticity decreases steeply at high and low temperature regions, the former being the melting point T_1 and the latter the second order transition point T_2 of the gel which will be discussed in details later. Between these two temperatures, T_1 and T_2, the gel-elasticity increases slowly with temperature.
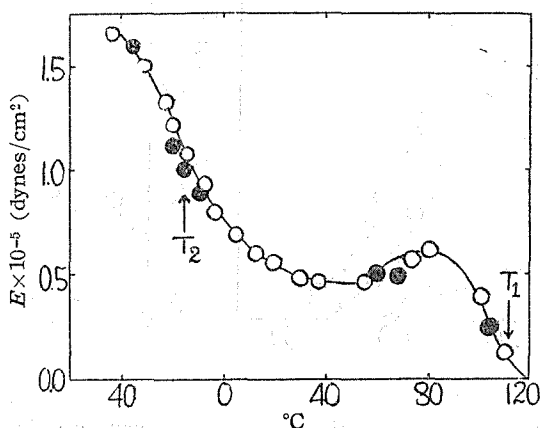

Fig. 3.
Temperature dependence of elasticity coefficient
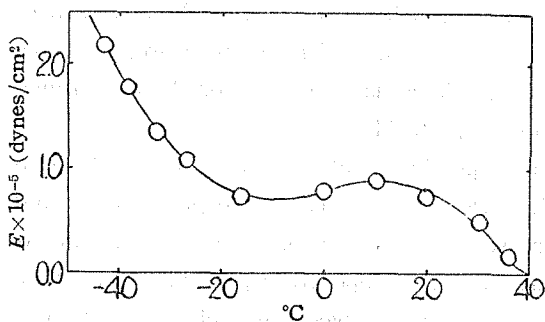of 16 % PVA (P=1680)-glycerol gel.

Fig. 4.
Temperature dependence of elasticity coefficient
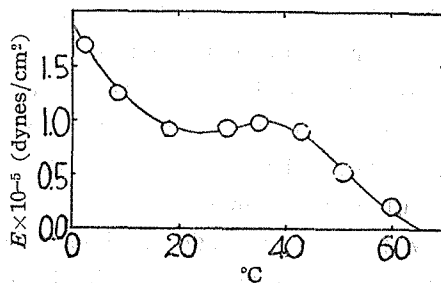of 7.0 % gelatin-glycerol gel.

Fig. 5.
Temperature dependence of elasticity
coefficient of 20 % PVA-a 0.75 %
congo red gel.

This typical form can also be seen in the gels of 7.0 % gelatin in 85 % glycerol[37] (Fig. 4), and 20 % polyvinyl alcohol[47] in water containing 0.75 % Congo red (Fig. 5).

The steep change of elasticity at lower temperature T_2 in the typical curve

does not appear in some gels. They are the gels of 4.5, 8.2 and 13.5 % polyvinyl alcohol ($\bar{P} = 1500$)[47] in water containing 1.5 % Congo red (Fig. 6), and 3.8 and 4.6 % amylopectin[47] in water (Fig. 7). In these gels, however, the elasticities also increase with increasing temperature at room temperature region.
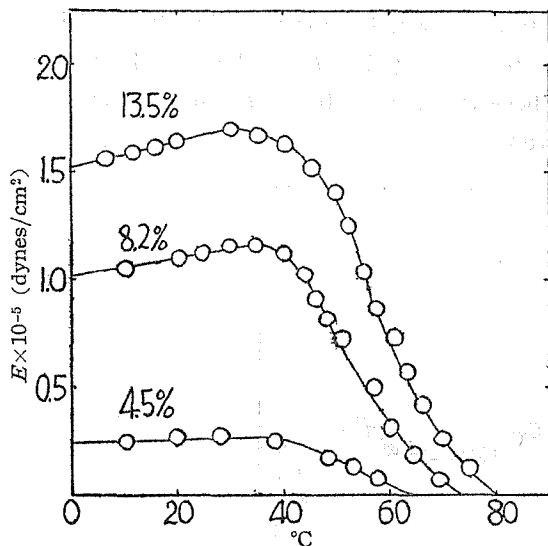

Fig. 6.
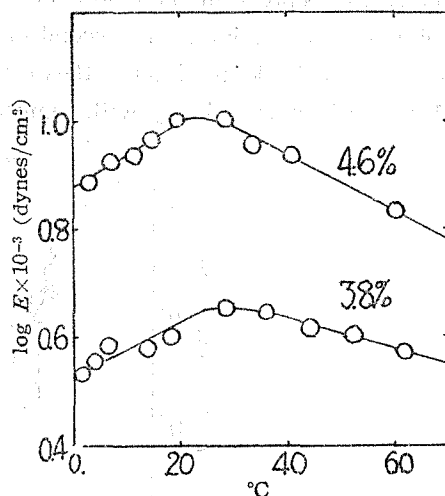Temperature dependence of elesticity coefficient of PVA-a 0.5 % congo red-H₂O gel.

Fig. 7.
Temperature dependence of elasticity coefficient of amylopectin-H₂O gel.

Therefore, it is reasonable to consider that the elasticities of these gels are rubber-like at these temperature regions. In other cases, these two temperatures, T_1 and T_2 in the typical curve of Fig. 3 approach each other and consequently the intermediate region, where the elasticity increases with temperature, becomes narrower and finally seems to disappear. This is the case for 1.06 % orange pectin gel[38] in saturated sucrose solution at pH 3 (Fig. 8).

The elasticity coefficient of the orange pectin gel always decreases with temperature in the whole range. In detail, however, it decreases steeply at high and low temperature regions, while it decreases more slowly or is almost constant at room temperature, and even in this case the two temperatures, T_1 and T_2, can be discriminated. We can find no essential difference between the gels in the typical form and this orange pectin gel, and so it may be reasonable to assume that the orange pectin gel is essentially rubber-like at room temperature and the elasticities of the hydrogels of agar and gelatin may also be rubber-like for the same reason.

These situations may be elucidated by the network mechanism of gel as stated by Ferry for gelatin gel[5]. Here, the structure of gel is considered to have a network as shown schematically in Fig. 9. This network has a certain number of cross-linkages formed by van der Waals forces between macromolecules. The
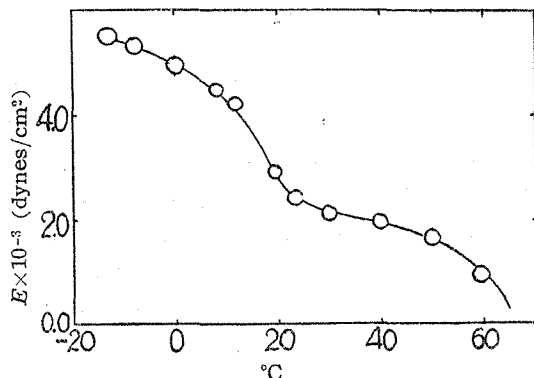
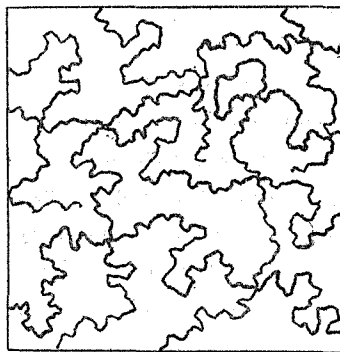Fig. 8. Temperature dependence of elasticity coefficint of 1.06 % pectin-H₂O gel.

Fig. 9. Network structure of gel.

elasticity of the gel is attributed to the thermal motion of the segments of these flexible macromolecules. So far as the rubber-like elasticity is concerned, the elasticity coefficient should be proportional to the absolute temperature and the number of the cross-linkages[27]. In the vulcanized rubber, the number of cross-linkages does not change with temperature because the linkages are "sulfur-bridge", a chemical binding, and so the elasticity increases over a wide range of temperature. In the reversible gel, however, the number of cross-linkages decreases with temperature by thermal dissociation, because the linkages are secondary bindings due to van der Waals forces[19]. Therefore, the elasticity of a reversible gel may apparently decrease with temperature when the decrease in cross-linkages overcomes the increase in rubber-like elasticity which should be proportional to the absolute temperature. Even in this case, the mechanism of the elasticity should be essentially the same as that of the elastic rubbers and differs from the case of the crystal.

The steep decrease of elasticity coefficient at lower temperature T_2 in Fig. 3 does not appear in the case of the hydrogels of agar, gelatin, polyvinyl alcohol and amylopectin as shown in Figs. 1, 2, 6 and 7. These facts may be understood by the following consideration. In such dilute hydrogels, the solvent, namely water, freezes at about 0° C and the gel-elasticity cannot be measured at lower temperature range where the steep decrease is expected to appear. On the contrary, in the gel of polyvinyl alcohol in glycerol, the solvent is supercooled far below its freezing point and the elasticity can be measured over a wider range of low temperature.

Most of the previous investigators studied only the hydrogel of agar or gelatin at a narrow temperature range and that is the reason why they did not find the positive temperature coefficient and the second order transition point of the gel-elaticity which prove the rubber-like elasticity of the gel. The significance of the second order transition of the gel will be discussed in detail in the next section.

2. THE SECOND ORDER TRANSITION OF THE GEL

As is well known,[15][36] the elasticity coefficient of high polymeric substance without solvent is about $10^{10} \sim 10^{11}$ dynes/cm² at ordinary temperature and its nature is energetic, but it decreases steeply to the value of about $10^7 \sim 10^8$ dynes/cm² at a certain temperature, the so-called second order transition point, and above this temperature the elasticity has been considered to be rubber-like. At the second order transition point, there occur some characteristic changes in the other properties such as heat capacity, volume expansion coefficient and dielectric constant.

The nature of the second order transition of high polymers has been interpreted from various points of view[16][17], and it is generally accepted that this transition is closely associated with the free rotation of segments in the macromolecule.

Above the second order transition point, the thermal energy of the segment motion overcomes the potential barrier and the internal rotation is set free. This internal free rotation makes the macromolecule flexible and the elasticity of high polymeric substance becomes rubber-like.

It may be reasonable to consider the inter- or intramolecular force affects the second order transition as well as the melting points, so that the second order transition point of a substance should be closely related to its melting point.

R. G. Beaman,[18] E. Jenckel[19] and N. Hirai[39] have pointed out independently that the ratio of the second order transition point to the melting point on the absolute scale is $0.6 \sim 0.7$ for many materials as shown in Table 1.

Table 1. Relationship between second order transition point T_2 and melting point T_1 of various materials.

Material	T_1 (°K)	T_2 (°K)	T_2/T_1
Polyethylene	388	205	0.53
Rubber	289	201	0.68
Nylon	~500	320	~0.64
Polystyrene	~500	355	~0.71
Polyvinyliden chloride	458	256	0.56
Ethyl cellulose	433	316	0.73
Cellulose acetate	576	337	0.59
Polyvinyl chloride	~500	348	~0.70
Polyvinyl alcohol	~570	353	~0.62
Polycapramide	458	336	0.73
n-Propyl alcohol	146	93	0.64
Glycerol	291	185	0.64
Phosphorus	317	195	0.62
Sodium thiosulfate	321	230	0.72
Boron trioxide	724	503	0.70

In such gels as are shown in Figs. 3, 4, 5, 8 and 10, the elasticity coefficients

decrease steeply at two certain narrow temperature ranges in the same manner as in the pure high polymeric substance, and this lower temperature region corresponds to the second order transition point of the gel as has been assumed in the previous section.
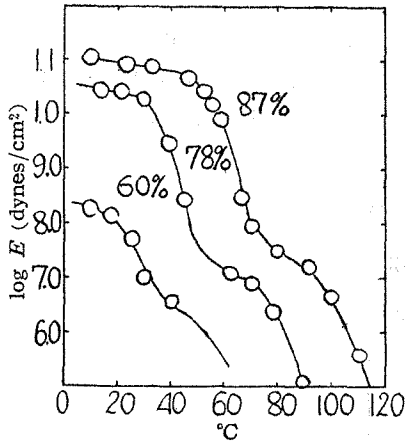

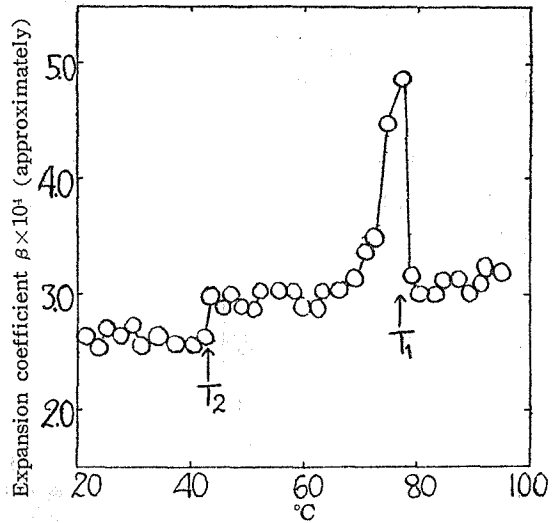Fig. 10. Temperature dependence of elasticity coefficient of concentrated gelatin-H_2O gel.

Fig. 11. Temperature dependence of volume expansion coefficient of 78% gelatin-H_2O gel.
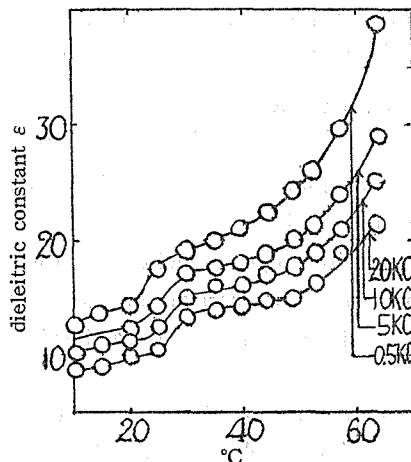

Fig. 12. Temperature dependence of dielectric constant of 69% gelatin-H_2O gel.

This assumption can be confirmed by many other experimental facts. The temperature dependency of the volume expansion coefficient of 78 % gelatin hxdrogel[41] is shown in Fig. 11. A steep increase in the expansion coefficient appears at 40° C. Similar results have been obtained by R. E. Neiman[20] for the expansion coefficients of 10 ~ 35 % gelatin gels. He has interpreted this anomaly

as a phase transition, but it should be attributed to the second order transition not only by its definition but by the fact that it agrees with the temperature where the abrupt fall in the elasticity coefficient of this gel can be observed as shown in Fig. 10.*

The temperture dependencies of the dielectric constant of 70% gelatin hydrogel[42] at various frequencies are shown in Fig. 12, where a discontinuous increase can be seen at about 25~30℃ in each curve. In Fig. 13, these temperatures where the elasticity coefficients, the volume expansion coefficients and the dielectric constants show abrupt changes, are plotted against the concentrations of gelatin gels. These points fall on almost the same curve, that is the second order transition of the gel.[42]
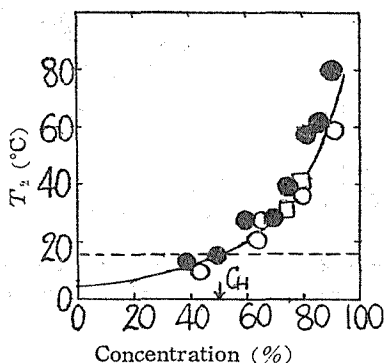

Fig. 13. Dependence of the second order transition
point T_2 of gelatin-H_2O gel upon concentration.
⬤, dielectric constant
◯, elasticity coefficient
☐, volume expansion coefficient

The second order transition point of gelatin gel falls with water content and reaches the room temperature at about 50 % water content as shown in Fig. 13. The elasticity of an ordinary hydrogel of gelatin at the concentration less than 50 % must be rubber-like at room temperature, because the elasticity is energetic below the second order transition point and rubber-like above this point as mentioned above.

These situations can be explained by the analogy of the second order transition of high polymer.[21] In a dilute gel, the solvent molecules separate the molecules or the segments of the high polymer from each other, and the attractive forces between them are weakened. This effect permits the free rotation of segment at lower temperature and finally the elasticity becomes rubber-like at room temperature.

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* A sharp peak which appears at about 80℃ in Fig. 11. may be attributed to the melting point of this gel, because the steep decrease at higher temperature in Fig. 10. is found at about 80℃.

3. THE DEPENDENCE OF THE GEL-ELASTICITY UPON THE CONCENTRATION

It has been frequently reported by many workers[2][5][22][23] that the elasticity co-efficient of gelatin hydrogel is approximately proportional to the square of the concentration. In this study, the elasticity coefficients were measured on many kinds of gels and over wider concentration ranges and it was found that the elasticity coefficient of the gel at room temperature is roughly proportional to the square of concentration at higher range than a certain concentration[31], C_o, of the gel, while to the 4 th power of concentration lower than C_o. In many cases, these exponents have to be taken as less by about 0.3^{46} than 2 and 4, respectively.

Therefore, the dependence of the elasticity coefficient E upon the concentration C of the gel can be represented by the following relations,[31][46]

$$\log E = \alpha + \beta \log C, \qquad \beta = 1.7 \sim 2, \text{ where } C > C_o, \qquad (1)$$

$$\log E = \gamma + \delta \log C, \qquad \delta = 3.7 \sim 4, \text{ where } C < C_o. \qquad (2)$$

We call the relation of equation (1) the square law of concentration. The values of α, β, γ, δ and C_o of various gels are shown[46] in Table 2. In this Table, C_G is the minimum concentration of gelation where the gel becomes sufficiently

Table 2. Summary of data obtained from gel-elasticity measurements.

No.	High Polymeric Substance	$M \times 10^{-4}$	Solvent	α	β	γ	δ	C_o (%)	C_G (%)	C_H (%)	Ref.
1	Agar	1.0	Water	8.8	1.8	13.1	3.7_3	0.85	0.2	25.	31
2	Agar	1.0	65% Sucrose-Water	8.1	1.7	10.9	3.7_5	5.0	0.8	—	39
3	Gelatin	6.0	Water	7.2	1.9	9.8	3.9	7.0	1.3	50.	2,5,31
4	Gelatin	6.0	85% Glycerol-Water	7.0	1.8	9.9	3.7_5	3.0	1.6	—	37
5	Gelatin	6.0	55% Sucrose-Water	7.4	1.8	10.3	3.7	2.9	1.3	—	39
6	Orange pectin	6.0	62% Sucrose-Water pH 3	7.6	1.7	11.2	3.7_5	1.6	0.5	—	38
7	Glucomannan	23.3	Water	6.9	1.7	9.5	3.9	8.	2.5	40	45
8	C.M.C.Na	3.6	Water	7.2	1.8	9.4	4.0	10.	2.	40	45
9	Amylopectin	30.	Water	5.9	1.8	8.2	4.0	7.	4.6	55	45
10	Nitrocellulose	15.8	Nitroglycerin	7.3	2.2	10.8	3.9_5	1.3	—	—	25
11	Nitrocellulose	15.8	Nitroglycol	7.2	2.2	10.6	3.9_5	1.9	—	—	25
12	Polyvinyl chloride	6.6	Dioctyl phthalate	7.7	1.5	8.9	3.5	25.0	2.0	50	26
13	Polyvinyl alcohol	8.4	85% Glycerol-Water	—	—	9.6_5	3.7_0	4.	2.	—	35
14	〃	7.4	〃	6.6	1.7	9.7_3	3.7_5	〃	〃	—	〃
15	〃	6.9	〃	6.7	1.7	9.6_3	3.7_5	〃	〃	—	〃
16	〃	5.8	〃	6.9	1.7	9.2_5	3.6_5	〃	〃	—	〃
17	〃	4.6	〃	—	—	9.1_4	3.6_5	〃	〃	—	〃
18	〃	2.6	〃	—	—	8.5_9	3.7_7	10.	4.	—	〃
19	〃	6.6	Congo red-Water	7.3	1.5	10.0	3.5	8.	4.	—	47
	Mean	—	—	7.2_4	1.8_0	—	3.7_8	—	—	—	—
	Swollen Rubber	—	Benzene	7.6	1.8	—	—	—	—	—	40

rigid to resist pouring. In many cases, C_G was found to be nearly equal to the concentration where the gel-elasticity coefficient becomes about 10^3 dynes/cm² and to be less than a half or one third of C_o. The column headed $\overline{M}$ in Table 2 contains the average molecular weights of the polymers determined by viscosity or osmotic pressure measurements.

The dependences of elasticity coeffcients of gelatin and agar hydrogels upon their concentration are shown[40] in Fig. 14 and 15, respectively. At extremely high concentration region, called xerogel, where the gel contains only less than 10~20 % of water, the elasticity deviates from the square law and increases steeply as much as some thousands of times. The concentration C_H, where the elasticity begins to deviate from the square law, is shown in Table 2 for various hydrogels.

Fig. 14. Dependence of elasticity coefficient of agar-H₂O gel upon concentration.
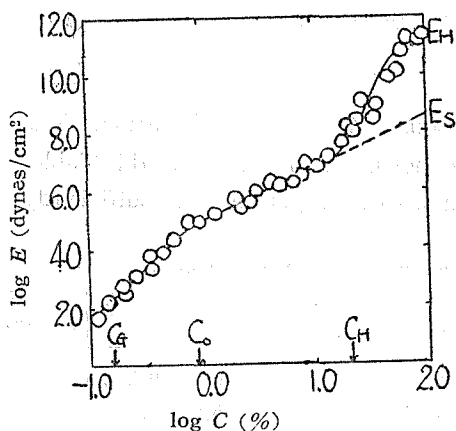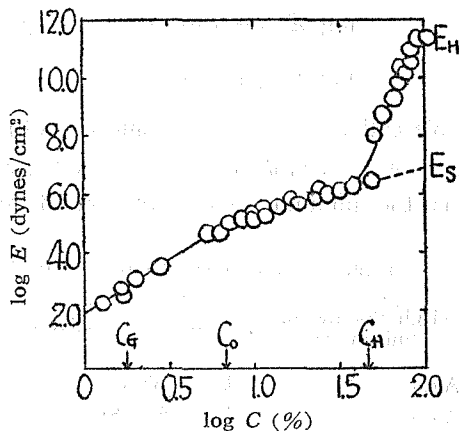

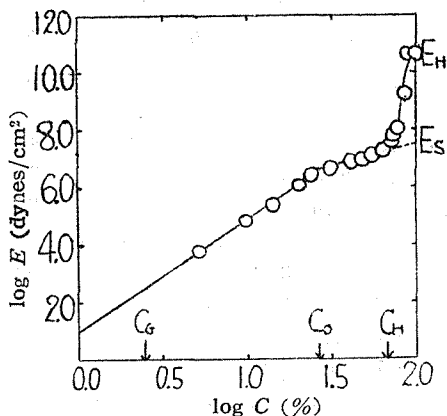Fig. 15. Dependence of elasticity coefficient of gelatin-H₂O gel upon concentration.

Fig. 16. Dependence of elacticity coefficient of rolyvinyl chloride-DOP gel upon its concentration (by A.T.Walter).
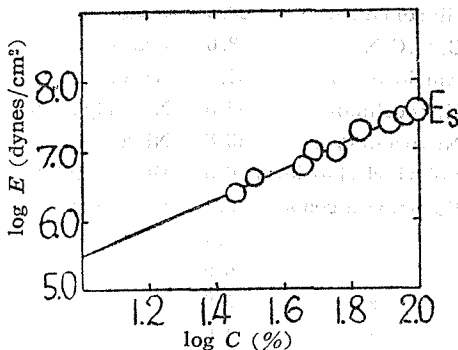

Fig. 17. Dependence of elasticity coefficient of rubber-benzene gel upon concentration.

Recently the similar results have been obtained by T. Sakurai and Y. Sato[24]

for nitrocellulose in nitroglycerin and nitroglycol, and A. T. Walter[25] for VYNW (vinyl chloride 96.4 %-vinyl acetate 3.6 % copolymer) in dioctyl phthalate (Fig. 16).

In these cases, the real values of elasticity coefficients, E_H, at 100 % gel are about 10^{11} dynes/cm², while the values of elasticity coefficients, E_s, extrapolated to 100 % gel with regard to the square law curve, are 4×10^8, 2×10^7 and 5×10^7 dynes/cm² for agar, gelatin and VYNW, respectively.

This elasticity coefficient, E_s, is the value for an imaginary gel, assumed to be brought to the state containing no solvent without changing the nature of the elasticity which obeys the square law of concentration. In other words, if all of the solvent could be removed from the gel without changing the nature of its elasticity, the elasticity coefficient of such gel should become E_s.

It is evident from equation (1) that the value of E_s should be equal to 10^{α} dynes/cm², α being shown in Table 2 for various gels. These values of E_s are $10^6 \sim 10^8$ dynes/cm² as can be seen in Table 2, and they agree nearly with the elasticity coefficient of elastic rubber which is well known to be of the order of 10^7 dynes/cm². The elasticity of vulcanized rubber swollen in benzene was measured at various degrees of swelling.[40] The dependence of the elasticity coefficient of this gel upon its concentration is shown in Fig. 17. As shown in Fig. 17, the square law of concentration is valid up to 100 % and this corresponds to the fact that the elasticity of rubber itself is rubber-like in the state containing no solvent. The values of α and β of this rubber-gel are 7.6 and 1.8, respectively, while the mean values of α and β of many gels are 7.2 and 1.8 as shown in Table 2. These facts confirm that the gel-elasticity is rubber-like at the concentration range where the square law holds.

On the other hand, the real elasticity coefficient of xerogel is about 10^{11} dynes/cm² and the energy elasticity coefficient of high polymeric substance has been calculated[26] theoretically to be about $10^{11} \sim 10^{12}$ dynes/cm². Moreover, the steep decrease in the elasticity coefficient with the decrease in the concentration can be seen at about 50 % of gelatin gel in Fig. 15, and this agrees with the concentration where the second order transition point of this gel falls to room temperature as shown in Fig. 13. These facts confirm that the elasticity of the xerogel at room temperature is energetic.

4. GOUGH-JOULE EFFECT OF THE GEL

In the rubber-like elasticity, work done by the elongation changes into heat which raises the temperature of the system. Actually, when a specimen of elastic rubber is elongated or contracted adiabatically, its heating or cooling can be detected with our lips. This phenomenon, called Gough-Joule (1857) effect, is also expected to be seen in the gel of high polymer, if its elasticity is rubber-like, but it has not been confirmed by any investigators up to the present.

The maximum elongation ratio is several hundred per cent for elastic rubber, but it was small for most gels which have been studied previously. Therefore, most of the gels could not be elongated enough to show the temperature change without breaking. This ratio, however, amounts to more than 100 % in the comparatively concentrated hydrogel of gelatin or polyvinyl alcohol containing a small amount of Congo red.

It was attempted[48] to detect the temperature changes for these gels, by using a circuit with a thermister whose sensibility is more than about 10^{-3} °C. The results obtained for the hydrogels of 20 and 30 % gelatin* and 35 and 50 % polyvinyl alcohol containing 0.5 % Congo red[48] are shown in Figs. 18 and 19 where
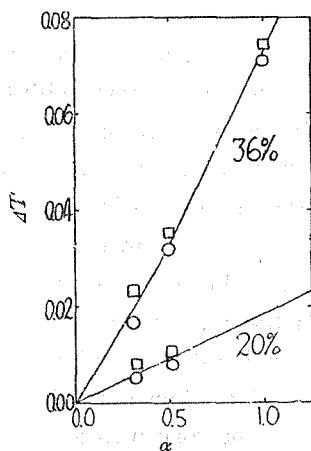
Fig. 18. Gough-Joule effect of
gelatin-H_2O gel.
□ elongation
○ contraction
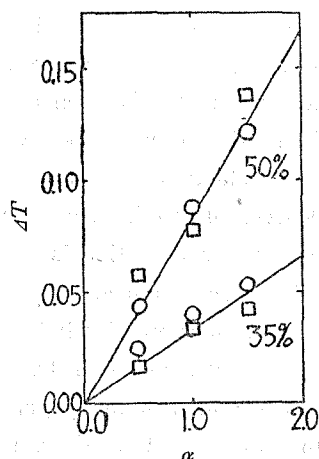
Fig. 19. Gough-Joule effect of
PVA-congo red gel.
□ elongation
○ contraction

the elongation ratio α is plotted as abscissa against the temperature change as ordinate.

Table. 3. Gough-Joule Effect of the Gel.

Gel	Conc. (%)	E (dynes/cm²)	ΔT_1	$E/\Delta T \times 10^{-7}$
Gelatin-H_2O	20	8. $\times 10^5$	0.020	4.0
//	36	2. $\times 10^6$	0.073	2.7
//	45	4. $\times 10^6$	0.080	5.0
PVA-0.5 % Congo red-H_2O	29	2.0×10^5	0.008₅	2.4
//	33	3.2×10^5	0.028	1.2
//	48	1.1×10^6	0.075	1.5
				$J = 4.2 \times 10^7$

ΔT_1 in Table 3 corresponds to the temperature change when $\alpha = 1$. It can be

* N. Hirai, unpublished.

easily derived* from the law of energy conservation that the absolute value of $E/\Delta T_1$ should be approximately equal to J (Joule constant, 4.2×10^7 ergs/cal) and opposite in sign at elongation and contraction for the rubber-like elasticity. In Figs. 18 and 19, only their absolute values are plotted. As shown in Table 3, the values of $E/\Delta T_1$ agree with the expectation in the order of magnitude. These data are not accurate enough to be discussed in details, but it can be concluded qualitatively that the elasticities of these gels are rubber-like.

5. THEORETICAL CONSIDERATION OF THE DEPENDENCE OF THE GEL-ELASTICITY ON CONCENTRATION AND MOLECULAR WEIGHT

In the previous sections, it has been concluded in various ways that the gel-elasticity is rubber-like at room temperature and ordinary concentration. On this basis, a qualitative discussion will be attempted below.

Now, it is generally accepted that gel is constructed by cross-linking between high polymeric molecules, that is a network structure. Since the cross-linkages prohibit the macro-Brownian movement but permit the micro-Brownian movement or the the thermal motion of the segments of macromolecule, the number of cross-linkages in unit volume must affect fundamentally the gel-elasticity.

If $\bar{n}$ is the number of such effective cross-linkages in unit volume, then according to the kinetic theory of rubber-like elasticity, the elasticity coefficient E can be expressed by the relation,[27]

$$E = 3 \bar{n} kT, \qquad (3)$$

where k is Boltzmann's constant and T is the absolute temperature. When the volume fraction of the polymer in the gel is v_2 and the polymer can be considered to be expanded to v_2^{-1} folds of its original volume, each macromolecule should be stretctched by a factor of $v_2^{-1/3}$ for 3 directions and so the elasticity coefficient increases by the same factor. Thus, we get for the elasticity coefficient of the gel,

$$E = 3 \bar{n} kT v_2^{-1/3}. \qquad (4)$$

As it is difficult to calculate the strict value of $\bar{n}$, an approximate estimation was attempted here. It is assumed that macromolecules in the gel can form a cross-linkage of the secondary binding only at some particular points, a sort of functional groups, in the molecules.

Let q be the number of functional groups in a macromolecule and p the degree of polymerisation when the macromolecule is considered to be a chain of monomers

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* Let be the work done by the elongation of a gel with unit volume and unit cross section, and c its specific heat which is about $0.5 \sim 1.0$ in these gels. In rubber-like elasticity, this work should change entirely into heat and then,

$$W = \frac{1}{2} E\alpha^2 = cJ\Delta T, \qquad \therefore E/\Delta T_1 = 2cJ \sim J.$$

which are the same in shape and volume as the solvent molecules. Then a parameter π is defined as follows,

$$\pi = p/q. \tag{5}$$

Since the value of π will increase in a good solvent or at high temperature but decrease in a poor solvent or at low temperature, it may be a sort of parameter representing the affinity of polymer to solvent.

If the molecular volume and density of the solvent are V_o and d_o, the molecular weight and density of the polymer are M and d, and the number of molecules of solvent and polymer in unit volume of the gel are n_1 and n_2 respectively, then we have

$$M = pv_od, \tag{6}$$

and

$$V_o(n_1+pn_2)=N_A, \tag{7}$$

where N_A is Avogadro's number. A cross-linkage can be formed when another functional group comes in one of Z sites, Z being the co-ordination number of a functional group. Then, the probability of a functional group to form the cross-linkage is given by

$$(\bar{n})_{f \cdot g}=Zqn_2/(n_2+pn_2)=Zv_2/\pi. \tag{8}$$

Since the average number $(\bar{n})_{mol}$ of cross-linkages in a macromolecule is q folds of $(\bar{n})_{f \cdot g \cdot}$, we obtain

$$(\bar{n})_{mol}=Zpv_2/\pi^2. \tag{9}$$

As shown in equation (9), the number of cross-linkages contained in a molecule decreases with concentration and in a dilute gel some molecules may have none or only one cross-linkage. These molecules do not contribute to the elasticity of the gel, since their macro-Brownian movements cannot be prohibited. It can be assumed that the macromolecules have to contain more than r cross-linkages in order to contribute to the gel-elasticity, and the number of molecules with more than $r+1$ cross-linkages is neglected in a sufficiently dilute gel.

Then the total number of cross-linkages contained in the molecules with more than r cross-linkages, can be calculated approximately as follows,

$$\bar{n} \approx \frac{1}{2}n_2r \; _qC_r(Zv_2/\pi)^r$$
$$\approx N_AZ^rp^{r-1}v_2^{r+1}/2(r-1)!\;\pi^{2r}V_o.$$

Thus, we get the general formula for E from equation (4),

$$E \approx 3RTZ^rp^{r-1}v_2^{r+2/3}/2(r-1)!\;\pi^{2r}V_o. \tag{10}$$

What value should be taken for r in equation (10). It has been known that, in the case of polymerisation condensation of polyester[25][29], a small amount of

trifunctional monomers such as glycerol is required to form a three dimensional network structure in the presence of large amount of bifunctional monomers such as ethylene glycol, and the number of cross-linkages of this network structure should be nearly equal to the amount of the trifunctional monomers. The situation may be analogous in the case of the gel formation. If it is granted that only the cross-linkages contained in the molecules with more than three crosslinkages contribute to the gel-elasticity, r in equation (10) should take the value 3.

Accordingly, we have

$$E \approx 3RTZ^3 p^2 v_2^{11/3}/4\pi^6 V_0. \tag{11}$$

Thus, the elasticity coefficient is expected to be proportional to the 3.67 th power or approximately the 4 th power of the concentration. As shown above, experimental results agree quite well with this expectation in the case of dilute gels.

When the concentration of the gel increases above a certain value C_0, all of the molecules may have a sufficient number of cross-linkages to prohibit the macro-Brownian movement and then all cross-linkages formed in the gel contribute effectively to the gel-elasticity. In this case, $r = 1$ in equation (10), and so we have

$$E \approx 3RTZv^{5/3}/2\pi^2 V_0. \tag{12}$$

Therefore, the elasticity coefficient of the gel at high concentration above C_0, is expected to be proportional to the 1.67 th power or about the square of the concentration and this is, in fact, the case as mentioned in § 3.
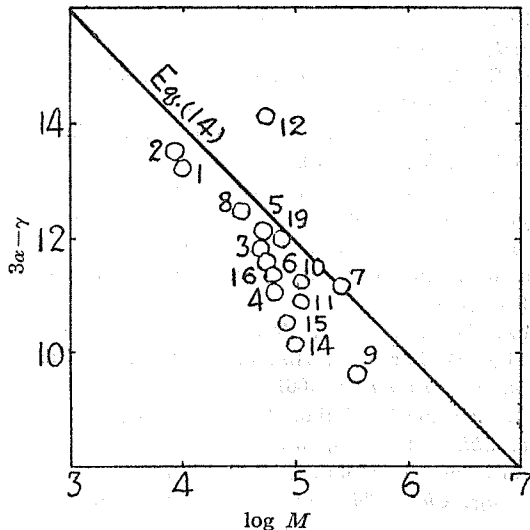

Fig. 20. $3\alpha - \gamma = 22.0 - 2 \log M$

Comparing equations (1), (2), (11) and (12), we obtain the following relations,

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$$\alpha = \log \,[3\,RTZ/2\,\pi^2\;V_o\,(d/d_o)^{5/3}], \hspace{3cm} (13)$$
and
$$\gamma = \log\,[3\,RTZ^3\,p^2/4\,\pi^6\;V_o\,(d/d_o)^{11/3}]. \hspace{2.5cm} (14)$$

Equations (13) and (14) give the physical meanings of α and γ which have been obtained experimentally in § 3 for various gels. Combining equations (6), (13) and (14), we get the relation between the gel-elasticity and the molecular weight of the high polymer as follows

$$3\alpha - \gamma = A - 2\,\log\,M,$$
where
$$A = 2\,\log\,[3\,\sqrt{2}\;RT(dd_o^2)^{1/3}] \approx 22.0. \hspace{2cm} (15)$$

This relation does not hold strictly for various gels listed in Table 2, but it agrees with observations in its general tendency and order of magnitude as shown in Fig. 20.

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