

## Deswelling of Gels by High Polymer Solutions

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Citation: *The Journal of Chemical Physics* **13**, 363 (1945); doi: 10.1063/1.1724050

View online: <http://dx.doi.org/10.1063/1.1724050>

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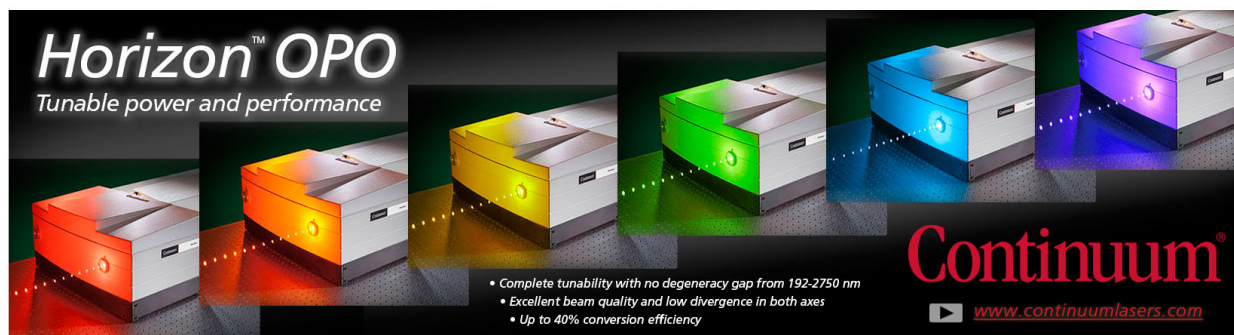
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## Deswelling of Gels by High Polymer Solutions

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(Received June 14, 1945)

When a cross-linked polymer initially swelled to its equilibrium volume in pure solvent is transferred to a solution of a high polymer in the same solvent and at the same temperature, the gel deswells. A quantitative treatment of this effect is given in terms of the Flory-Rehner theory of the thermodynamic properties of gels, and the Flory-Huggins theory of thermodynamics of high polymer solutions. The extent of deswelling depends on the molecular weight and concentration of the solute, on the

solvent-polymer interactions, and on the degree of cross-linking in the gel. It thus offers in principle a new method for determination of the number average molecular weight of the solute. Various calculations are presented to show the extent of deswelling under given conditions. Finally, some experimental data is offered to demonstrate determinations of molecular weights, using styrene-divinylbenzene copolymer gels and polystyrene solutions.

## INTRODUCTION

IT is well known that when certain high molecular weight materials are placed in a suitable solvent they swell to an equilibrium value determined by the solvent, the temperature, and the nature of the polymer. These polymers belong to two general types: (a) linear polymers which swell to a limited extent in one solvent but which can dissolve if the solvent and/or the temperature is suitably chosen; (b) three-dimensional polymers whose maximum swelling is limited by a primary valence network. An example of the type (a) is gelatin whose equilibrium swelling characteristics first received a rational explanation by Proctor and Wilson.<sup>1</sup> Haller<sup>2</sup> has discussed swelling pressure as a function of energy and entropy changes on dilution. Gee<sup>3</sup> has furnished a theory for equilibrium swelling based on entropy and heat of mixing effects. More recently Tobolsky<sup>4</sup> has treated the process of dissolution or "melting" of these soluble gels.

Frenkel<sup>5</sup> proposed that equilibrium swelling for three-dimensional gel structures occurs when the osmotic pressure is equal to the elastic reaction of the network chains. Flory and Rehner<sup>6</sup>

then provided a mathematical formulation for Frenkel's fundamental idea in terms of modern concepts of the thermodynamic behavior of high polymer systems. They included both the entropy and the heat of mixing effects. In particular, they showed that the activity,  $a_{1g}$ , of the solvent within the gel is given by

$$\ln a_{1g} = \mu_g v_{2g}^2 + \ln(1 - v_{2g}) + v_{2g} + (\rho V_1/M_c)(v_{2g})^{1/2}, \quad (1)$$

where  $v_{2g}$  is the volume fraction of polymer in the swollen gel,  $\rho$  is the density of the polymer,  $V_1$  is the molar volume of the solvent,  $M_c$  is the molecular weight of the polymer between points of cross-linkage, and  $\mu_g$  is the constant providing for interaction between polymer and solvent. This notation is similar to that employed by Flory and Rehner except for the subscript  $g$  which is used to identify the gel phase, and for the substitution of  $\mu_g$  in place of their  $K/2$ .  $\mu_g$  is used here in keeping with Huggins'  $\mu_1$  constant<sup>7</sup> to represent the polymer-solvent interaction term for soluble polymer systems. Flory and Rehner state that equilibrium swelling of a three-dimensional gel occurs when the partial molal free energy of dilution,  $\Delta\bar{F}_1$ , is zero, and hence when

$$M_c = -\rho V_1(v_{2g0})^{1/2} / [\mu_g v_{2g0}^2 + \ln(1 - v_{2g0}) + v_{2g0}], \quad (2)$$

$v_{2g0}$  is now the volume fraction of polymer in the swollen gel which is in equilibrium with pure solvent. Since  $v_{2g0}$  can be measured experi-

<sup>1</sup> H. R. Proctor and J. A. Wilson, *J. Chem. Soc.* **109**, 307 (1916).

<sup>2</sup> W. Haller, *Kolloid Zeits.* **56**, 262 (1931).

<sup>3</sup> G. Gee, *Trans. Faraday Soc.* **38**, 276, 418 (1942); *I.R.I. Trans.* **18**, 266 (1943).

<sup>4</sup> A. Tobolsky, *J. Chem. Phys.* **11**, 290 (1943).

<sup>5</sup> J. Frenkel, *Acta Physicochim.* **9**, 235 (1938); *Rub. Chem. Tech.* **13**, 264 (1940).

<sup>6</sup> P. J. Flory and J. Rehner, Jr., *J. Chem. Phys.* **11**, 521 (1943).

<sup>7</sup> M. L. Huggins, *Ann. N. Y. Acad. Sci.* **44**, 431 (1943).

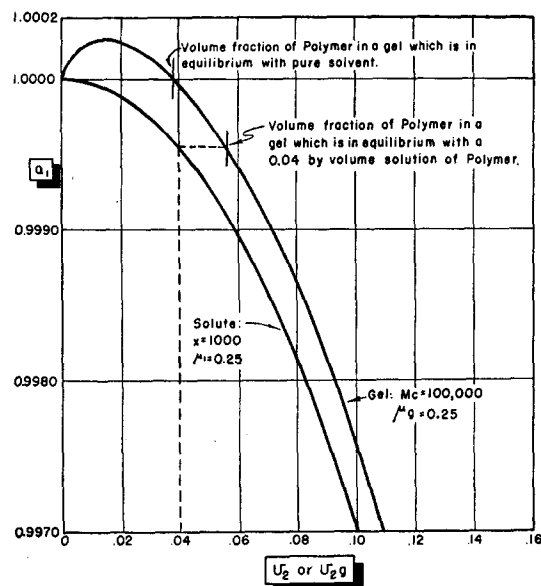


FIG. 1. Dependence of solvent activity,  $a_1$  (or  $a_{1g}$ ), on volume fraction,  $v_{2g}$ , of network polymer (upper curve); and on volume fraction,  $v_2$ , of solute (lower curve).

mentally on a given sample, and since  $\mu_g$  can be determined from swelling values at several temperatures, it is thus possible to calculate the extent of cross-linking as expressed by  $M_c$ .  $M_c$  is, therefore, a characteristic constant for a given gel sample while  $\mu_g$  is unique for a fixed gel-solvent system at a given temperature.  $\mu_g$  accounts for the variation in equilibrium swelling volume with different types of solvents and with temperature. Staudinger, Heuer, and Husemann<sup>8</sup> have reported numerous results on the swelling of styrene-divinylbenzene copolymers in a variety of solvents. Their results attest to the importance of  $\mu_g$  term in Eq. (1), as well as offering qualitative confirmation of the numerical relationship involved.

The cross-linking agent used throughout this report consisted of the three isomers of divinylbenzene diluted with the three isomers of ethylvinylbenzene. This mixture usually contained from 30 to 40 percent of divinylbenzene, with the meta-isomer predominating. Huggins<sup>7</sup> has calculated  $\mu_1$  for toluene-polystyrene solutions to be 0.44, and we assume that  $\mu_g$  is also 0.44, when toluene is used for styrene-divinyl benzene gels. The validity of this assumption must still be

<sup>8</sup> H. Staudinger, W. Heuer, and E. Husemann, Trans. Faraday Soc. 32, 323 (1936).

justified by some experiments to determine how nearly  $\mu_g$  is the equivalent of  $\mu_1$ . Alfrey and coworkers<sup>9</sup> have shown, for example, that  $\mu_1$  for toluene-polystyrene varies with the temperature at which the styrene was polymerized. It may be that the presence of traces of cross-linking agents will alter the significance of this interaction constant, even when the cross-linking agent is chemically similar to the main polymer constituent. The principal cause for a difference between  $\mu_1$  and  $\mu_g$  is probably the restrictions imposed on the possible number of configurations due to cross-links. This effect is likely small for a slightly cross-linked gel.

### DESWELLING OF GELS BY HIGH POLYMER SOLUTIONS

There is now an interesting consequence of the swelling phenomena outlined above. If a swollen gel in equilibrium with pure solvent is transferred to a solution of a high polymer in the same solvent and at the same temperature, the gel will deswell. The polymer in solution prefers to be in a more diluted state and can do so only by extracting solvent from the swollen gel. The elastic contraction of the network chains within the gel assists in this process until a new swelling equilibrium obtains. The extent of deswelling will depend primarily on the degree of cross-linking in the gel, on the concentration and

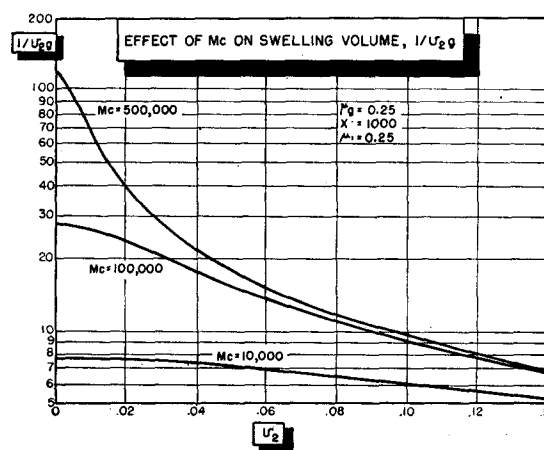


FIG. 2. Decrease in swelling volume,  $1/v_{2g}$ , with increasing amounts of solute,  $v_2$ , for three gels of different degrees of cross-linking.

<sup>9</sup> T. Alfrey, A. Bartovics, and H. Marks, J. Am. Chem. Soc. 65, 2321 (1943).

molecular weight of the dissolved polymer, and on the solvent-polymer interactions, as expressed by  $\mu_g$  and  $\mu_1$ . As one example, a styrene - 0.05 percent divinylbenzene gel which had swelled to 13.8 its dry volume in pure toluene, decreased to 7.7 times its dry volume in a 10 percent by weight solution of polystyrene in toluene. The polystyrene solute had a molecular weight of 302,000 by light scattering.<sup>10</sup> Other examples of the extent of deswelling will be apparent later.

After we had observed such deswelling action, a survey of the literature revealed that this behavior was quite well known. In fact, Blow and Stamberger<sup>11</sup> in their classical investigation of the deswelling of rubber gels, referred to it as the so-called *Bodenkörper* effect, apparently in allusion to earlier work by Ostwald on gelatin. They interpreted this general effect qualitatively on the basis of osmotic pressure, but did not give

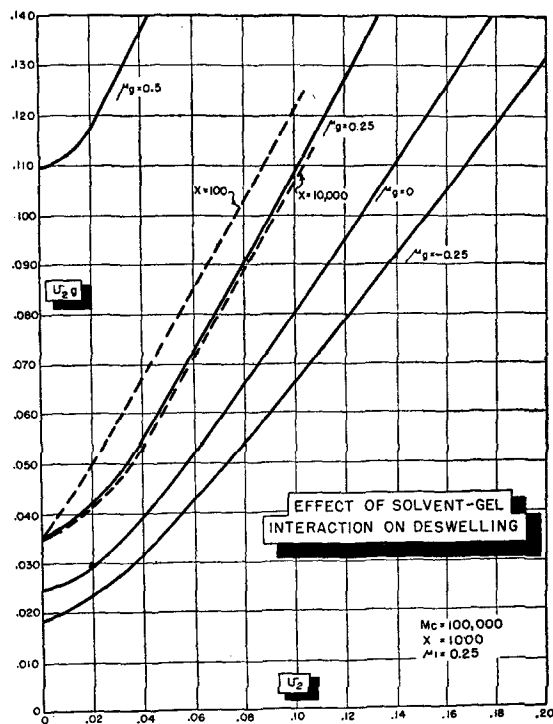


FIG. 3. Increase in network polymer concentration,  $v_{2g}$ , with increasing solute concentration,  $v_2$ , for different values of  $\mu_g$ . The upper and lower dashed curves (with  $\mu_g = 0.25$ ) illustrate the effect of a very low and a very high molecular weight solute.

- <sup>10</sup> P. Debye, J. App. Phys. **15**, 338 (1944); P. M. Doty, B. H. Zimm, and H. Mark, J. Chem. Phys. **13**, 159 (1945).  
<sup>11</sup> C. M. Blow and P. Stamberger, Rec. Trav. Chim. **48**, 681 (1929).

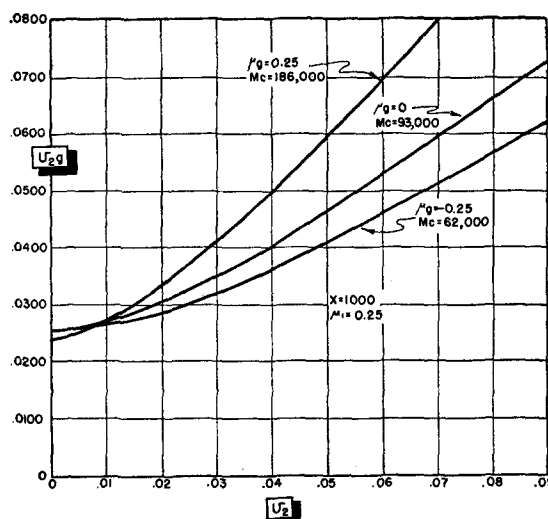


FIG. 4. Dependence of  $v_{2g}$  on  $v_2$  for three gels of different  $M_c$  and  $\mu_g$  having approximately the same degree of swelling in pure solvent.

a quantitative treatment. More recently, Powers and Robinson<sup>12</sup> observed that the swelling of synthetic rubbers by oil was smaller in oils which contained polyisobutylene as a viscosity index stabilizer.

Because of current advances in theoretical knowledge concerning the thermodynamics of high polymer systems, it is now relatively simple to provide a quantitative treatment for this deswelling action. It suffices merely to correlate the Flory-Rehner<sup>6</sup> theory of gels with the Huggins<sup>13-15</sup> and Flory<sup>16</sup> treatment of high polymer solutions. Huggins and Flory have shown that the activity of the solvent in contact with solute is given by

$$\ln a_1 = \ln(1 - v_2) + (1 - 1/x)v_2 + \mu_1 v_2^2, \quad (3)$$

where  $v_2$  is the volume fraction of polymer in solution, and  $x$  is the ratio of the volume of a polymer molecule to the volume of a solvent molecule. Flory<sup>16d</sup> has demonstrated that this equation is also valid for a heterogeneous solute if  $x$  is replaced by its number average value  $\bar{x}_n$ .

The criterion for the new swelling equilibrium

- <sup>12</sup> P. O. Powers and H. A. Robinson, Ind. Eng. Chem. **34**, 614 (1942).  
<sup>13</sup> M. L. Huggins, Ann. N. Y. Acad. Sci. **43**, 1 (1942).  
<sup>14</sup> M. L. Huggins, J. Phys. Chem. **46**, 151 (1942).  
<sup>15</sup> M. L. Huggins, J. Am. Chem. Soc. **64**, 1712 (1942).  
<sup>16</sup> P. J. Flory, J. Chem. Phys. (a) **9**, 660 (1941); (b) **10**, 51 (1942); (c) **12**, 114 (1944); (d) **12**, 425 (1944).

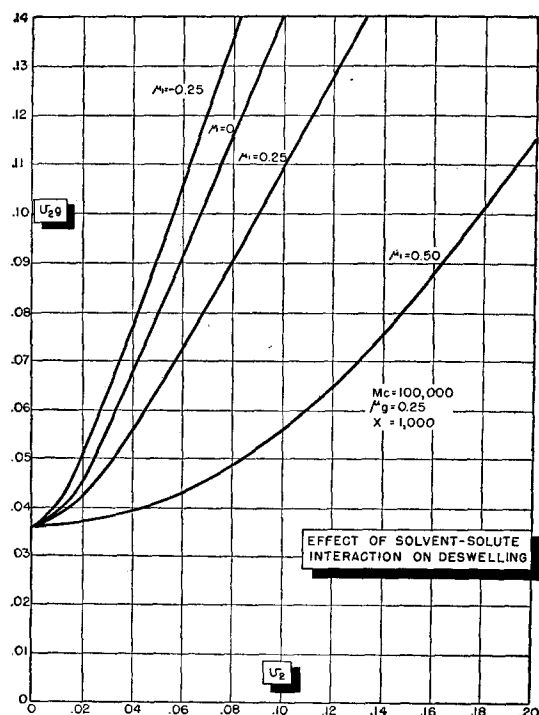


Fig. 5. Effect of  $\mu_1$  on deswelling action. By comparison with Fig. 4 it is seen that  $\mu_1 \ll 0.5$  and  $\mu_g \approx 0.5$  favor deswelling.

established when a swollen gel is transferred from pure solvent to a solute system should be given by equating the activity of the solvent within and without the gel. The solvent will leave the phase in which its activity is higher until this equality obtains. It will be realized that this same equilibrium swelling volume should also prevail if the gel is swollen for the first time in the presence of a solute.

The deswelling action can be seen clearly by examining Fig. 1 which is a plot of solvent activity as a function of polymer concentration. The top curve, referring to the gel phase, and the bottom curve, referring to the solute system, were obtained by substituting numerical values in Eqs. (1) and (3), respectively. The gel is in equilibrium with pure solvent when the activity of the solvent is unity, and hence when  $v_{2g}$  is 0.037. If this gel is now transferred to a 4 percent by volume solution of polymer, it will shrink by moving down along the upper curve until the activity of the solvent is the same in both phases, as indicated by the horizontal dotted line.  $v_{2g}$  will now be 0.056. In general, for a finite molecular

weight of the solute and for  $\mu_1$  less than 0.5, the curve for the gel will always be above the solute curve.  $v_{2g}$  will always be greater than  $v_2$ , although the two curves approach each other and finally meet for  $v_2 = v_{2g} = 1$ . When  $\mu_1$  is larger than  $\mu_g$ , the activity *versus* concentration curves will intersect for  $v_2$  less than unity. The general condition for this is that  $a_1 = a_{1g}$ , and  $v_2 = v_{2g}$ , whence

$$(\mu_1 - \mu_g)v_2^2 = v_2/x + (\rho V_1/M_c)v_2^{3/5}. \quad (4)$$

Since the right-hand side of the equation must be positive,  $\mu_1$  must be greater than  $\mu_g$ . In case  $x$  is extremely large,

$$v_2 = [\rho V_1/(\mu_1 - \mu_g)M_c]^{3/5} \quad (5)$$

gives the abscissa of the point of intersection. The gel will still deswell under such conditions, although  $v_{2g}$  may be greater than, equal to, or less than  $v_2$ , depending on the value of  $v_2$ . Since  $\mu_1 > \mu_g$  is a very unfavorable condition for deswelling, as will be seen presently, this case of intersecting activity curves is of slight practical interest.

To illustrate further the extent of deswelling action, a series of curves shown in Figs. 2-5 have been prepared, using essentially the graphical method indicated in Fig. 1. Certain arbitrary values were chosen for the parameters such as to illustrate cases that might arise in practice. Three gels of different degrees of cross-linking were selected, with  $M_c = 10,000$ , 100,000, and 500,000, and with  $\mu_g$  ranging from -0.25 to 0.5.  $\rho V_1$  was made equal to 100. The soluble polymers were characterized by  $x = 100$ , 1000, and 10,000. In the case of polystyrene dissolved in toluene this would correspond approximately to molecular weights of  $10^4$ ,  $10^5$ , and  $10^6$ .  $\mu_1$  ranged from -0.25 to 0.50. The complete expressions for solvent activity (Eqs. (1) and (3)) were employed in these calculations since the expansion of the logarithms would require the use of too many terms in the series, particularly for the gel. In making some of the cross comparisons, a typical polymer was chosen as  $X = 1000$ ,  $\mu_1 = 0.25$ , while a typical gel was assumed as  $M_c = 100,000$ ,  $\rho V_1 = 100$ , and  $\mu_g = 0.25$ .

In general we can equate the logarithms of the solvent activities given by Eqs. (1) and (3). If we represent the negative of the right-hand side of

Eq. (1) by the swelling function,  $S(v_{2g})$ , and if we expand logarithms and combine terms in Eq. (3), we obtain for  $\ln a_{1g} = \ln a_1$ :

$$S(v_{2g}) = v_2/\bar{x}_n + (0.5 - \mu_1)v_2^2 + v_2^3/3 + \dots \quad (6)$$

$S(v_{2g})$  contains the constant quantity,  $\rho V_1/M_c$ , which can be evaluated numerically from swelling experiments in pure solvent. However, Flory has suggested<sup>17</sup> that if  $\rho V_1/M_c$  is replaced by its algebraic equivalent, as given in Eq. (2), then

$$S(v_{2g}) = (0.5 - \mu_g)2v_{2g^0}\Delta + v_{2g^0}^2\Delta + \dots \quad (7)$$

where  $v_{2g^0}$  is the volume fraction of polymer in the gel which is in equilibrium with pure solvent, and  $\Delta = v_{2g} - v_{2g^0}$ . Substituting in Eq. (7) and rearranging gives

$$\frac{\Delta}{v_2} = \frac{1/\bar{x}_n + (0.5 - \mu_1)v_2 + \dots}{2(0.5 - \mu_g)v_{2g^0} + v_{2g^0}^2/(1 - v_{2g^0})} \quad (8)$$

This equation predicts that the change in swelling per unit of dissolved polymer is greater when  $\bar{x}_n$  and  $v_{2g^0}$  are small,  $\mu_1 \rightarrow 0$ , and  $\mu_g \rightarrow 0.5$ . In other words, a very loose or slightly cross-linked gel should be swelled in a medium which is a poor solvent for the network polymer but a good solvent for the solute ( $\mu_1 < \mu_g$ ).

In practice there are physical limitations which dictate to a large extent what gels and solvents may be employed. Gels swollen to 25 or more times their dry volume deform readily and are difficult to handle. Moreover, with poor solvents (large  $\mu_g$ ) loose gels become quite tacky and will rupture easily. Eqs. (6) and (8) nevertheless provide a basis for molecular weight determinations from deswelling experiments. Before discussing this subject there are several interesting questions which should first be considered.

#### PERMEATION OF SOLUTE INTO THE GEL

In the course of some experimental studies certain discrepancies were noted which suggested that soluble polymer might be permeating into the gel. For instance, a divinyl copolymer originally swelled in toluene for an

insufficient time to reach equilibrium was then transferred to a polystyrene solution. Instead of deswelling the sample increased in weight beyond what was predicted as its equilibrium value. On removal of the specimen to pure toluene it deswelled to its correct equilibrium volume.

It is not surprising that polymer molecules, especially those of low molecular weight, could permeate the loose structure of a swollen gel. Physically, however, if the gel deswells on being placed in a solute, the stream of solvent leaving the gel should offset the tendency for polymer to migrate into the gel. Alternately, if a dry gel is swollen for the first time in contact with a solution, then solute could be carried into the gel rather easily. Disregarding such diffusion currents caused by the bulk movement of the solvent, the diffusion of the solute would be relatively slow. Moreover, the concentration of polymer in the gel (in the form of network chains) will usually be higher than the concentration of soluble polymer in the external solution. Thus the effective concentration gradient causing diffusion of solute molecules might be extremely small.

Fortunately Flory<sup>17</sup> was able to provide a positive statement concerning the effect of such permeation on the swelling behavior of the gel. He showed that even if the polymer does enter the gel, its influence on swelling will be negligible except when the molecular weight of the solute is extremely low and/or when the degree of swelling is extremely high. Specifically, this effect can be neglected if  $(x/V_0)$  is greater than 5.  $x$  is again the volume ratio of polymer to solvent molecule, and  $V_0$  is the swelling volume ( $= 1/v_{2g}$ ) in pure solvent. Since  $V_0$  would likely never exceed 50 because of difficulties in handling such loose gels, this criterion sets a limit of  $x = 250$ , corresponding roughly to a molecular weight of 25,000. Actually, the smaller the molecular weight of the polymer, the smaller can  $V_0$  be and still furnish good sensitivity. In practice then, this restriction is not a severe one. If, however, a weighing method is used, the extra weight of the solute in the gel would contribute a minor error.

We have referred thus far to the deswelling action of high polymer solutes. Any solute which lowers the activity of the solvent will show this

<sup>17</sup> I am indebted to Dr. Flory for the privilege of discussing this problem with him, and for his subsequent derivation of several equations which are used here with his permission.

deswelling action initially. Eventually, however, a low molecular weight solute would permeate the gel and the problem would reduce to one of mixed solvents. It seems convenient to choose Flory's critical condition,  $(x/V_0) > 5$ , as a definition of the type of solute with which we are here concerned. Flory has suggested, in the case of a heterogeneous polymer, that even though the average sized molecule will not cause trouble by permeation, yet some of the smaller species present may do so. This is a selective effect which might be likened to the diffusion of low molecular weight species through the membrane in an osmotic pressure experiment.

Another possible disturbing influence might be the effect of hydrostatic pressure on the swelling volume of these gels. All of the experiments reported here were carried out with a small head of solvent (approximately 5 cm). At equilibrium swelling, the swelling pressure (defined by Posnjak<sup>18</sup> as the pressure needed to prevent further swelling) is zero. Hence weak gels should be quite sensitive to small changes in pressure under conditions of a deswelling experiment. Preliminary experiments on gels swelling 20-fold in toluene showed a slight decrease in swelling volume as the head of liquid was increased from 1 to 100 cm. For most purposes this effect can be neglected.

Thus far we have stressed the use of cross-linked gels for this work. The soluble type of gels mentioned in the introduction should also offer some possibilities for investigation. Bronstead and Volqvartz, for example, have studied the swelling of polystyrene in alkyl laurates.<sup>19</sup> This system is characterized by large values of  $\mu_1$ .<sup>7</sup> Polymers for which the alkyl laurates are good solvents ( $\mu_1$  small) would be expected to deswell these polystyrene-alkyl laurate gels. Here the action would not arise from a tendency for network contraction, but would result largely from heat of dilution effects as expressed in experimental values of  $\mu_g$  and  $\mu_1$ . Gee's theory of swelling would be applicable here.<sup>3</sup> Such a system would be subject to more experimental restric-

tions in choosing solvents, than is the case with a cross-linked gel.

#### MOLECULAR WEIGHTS OF HIGH POLYMERS FROM THE DESWELLING OF GELS

This present investigation of gels was prompted by a search for new methods of measuring molecular weights of polymers. It was inspired, not by the work of Blow and Stamberger which was unknown to us at the time, but by some biological considerations. Briefly, it is believed that the mechanism through which simple salt solutions destroy bacteria is an osmotic dehydrolysis of the microorganism.<sup>20</sup> This suggested that bacteriocidal action might give a quantitative measure of osmotic pressure. H. deVries, around 1884, was able to compare the osmotic pressure of various aqueous solutions by their action on the structure of plant cells, while Hamberger, in 1886, used red blood cells for the same purpose. Glasstone has recently called attention to both of these techniques.<sup>21</sup> Aside from the possible restriction of such methods to aqueous systems, it seemed doubtful if an absolute measure of the osmotic pressure could be obtained. A cross-linked polymer, swellable in organic liquids, scientifically reproducible, large enough to be handled and weighed with precision, and finally, as we have seen, amenable to mathematical investigation, presented itself as a substitute for bacteria or plant cells or red blood corpuscles. The theoretical treatment given above, and some experimental results which will now be presented, show that it is possible, both in principle and in performance, to measure molecular weights of polymers by the osmotic deswelling action of their solutions.

For this purpose we divide Eq. (6) by  $v_2$  and transpose one term to give:

$$S(v_{2a})/v_2 - v_2^2/3 = 1/\bar{x}_n + (0.5 - \mu_1)v_2 + \dots \quad (9)$$

This equation implies that if gel samples are swelled to equilibrium in pure solvent and then transferred to several solutions of polymer at different concentrations in the same solvent, the

<sup>18</sup> E. Posnjak, *Kolloidchem. Beihefte* **3**, 417 (1912); see also P. J. Flory and John Rehner, Jr., "Effect of Deformation on the Swelling Capacity of Rubber," *J. Chem. Phys.* **12**, 412 (1944).

<sup>19</sup> J. N. Bronstead and K. Volqvartz, *Trans. Faraday Soc.* **35**, 576 (1939).

<sup>20</sup> R. E. Buchanan and E. I. Fulmer, *Physiology and Biochemistry of Bacteria* (Williams and Wilkins, Baltimore, 1930), Vol. II, p. 195ff.

<sup>21</sup> Samuel Glasstone, *Textbook of Physical Chemistry* (D. Van Nostrand Company, Inc., New York, 1940), p. 651-3.

TABLE I. Deswelling of 0.033 percent divinylbenzene—styrene gels by toluene solutions of polystyrene at 24°C.

Gel no.	Maximum weight ratio in pure toluene <sup>a</sup>	Stabilized weight ratio in pure toluene <sup>b</sup>	Volume concentration of polystyrene <sup>c</sup> $v_2$	Corrected weight ratio in solution <sup>d</sup>	$v_{20}$ <sup>e</sup>	$\frac{V_1}{M_c} \times 10^6$	$S(v_{20}) \times 10^7$	$\frac{S(v_{20})}{v_{20}^2}$	
								$v_{20}$	3
236	20.58	18.11	0	20.10	0.0414	368			
239	20.71	18.11	0.00475	19.79	0.0420		33		69.5
241	20.79	18.10	0.00946	19.27	0.0432		107		110
243	20.52	18.05	0.0141	18.45	0.0451		227		154
252	20.51	18.05	0.0187	17.60	0.0473		379		191
246	20.53	17.94	0	19.92	0.0420	375			
237	20.51	17.97	0.0231	16.35	0.0510		631		255
233	20.30	17.92	0.0276	15.46	0.0540		880		294
244	20.41	17.84	0	19.71	0.0421	378			
250	20.21	17.88	0.0318	14.26	0.0585		1285		368
249	20.63	17.89	0.0361	13.40	0.0623		1677		422
240	20.51	17.77	0.0447	12.38	0.0676		2287		445

<sup>a</sup> Based on original dry weight of gels (approximately 0.27 g).<sup>b</sup> After leaching gels for 4 months in toluene at 24°C.<sup>c</sup> Corrected for dilution by toluene from gels.<sup>d</sup> Calculated from weight swelling ratio in solution after assuming that gels had lost 10 percent of their original weight as soluble material.<sup>e</sup> Volume fraction corresponding to corrected weight ratio in solution.

Note: Swelling was followed by removing sample from solvent or solution, rolled gently on Whatman Filter Paper no. 3, and weighed in a weighing bottle.

resultant deswelling data can be so handled as to yield a straight line permitting an accurate extrapolation to infinite dilution of the solute. The slope of this line measures the interaction,  $\mu_1$ , between solvent and solute. The intercept of this line is inversely proportional to the number average volume ratio,  $\bar{x}_n$ , between solute and solvent molecules. Hence it is inversely proportional to the number average molecular weight,  $\bar{M}_n$

$$\bar{M}_n = \bar{x}_n V_1 d_2,$$

where  $V_1$  is again the molal volume of the solvent and  $d_2$  is the density of the solute. The general agreement in form between Eq. (9) and the extrapolation method successfully employed for osmotic pressure measurements<sup>15</sup> is complete in every detail, except for some obvious numerical constants. Eq. (8) also furnishes a method for extrapolating deswelling data to infinite dilution. We shall employ Eq. (9) later because it involves no approximations other than those implicit in Eqs. (1) and (3).

Deswelling experiments therefore appear to offer a relatively convenient method of determining molecular weights of polymers. This technique is simply a variation of the osmotic pressure method. The swollen gel acts in effect like the membrane in an osmometer, allowing solvent molecules to diffuse freely through while

retarding at least the larger polymer molecules. Contrary to usual osmotic experiments, the solvent moves from the more concentrated to the more dilute system (except for some special cases mentioned earlier). Moreover, the "membrane" has a definite interest in how many solvent molecules are transported, the extent of this interest being expressed by the two characteristic gel constants  $M_c$  and  $\mu_0$ .  $M_c$  is known from a single swelling measurement according to Eq. (2);  $\mu_0$  is found from swelling measurements at several temperatures through the use of Eq. (15') of reference 6, or from swelling experiments in a solution of known activity.

A number of experiments have been carried out in an effort to verify Eq. (9). These experiments have served mainly to emphasize two disturbing properties of slightly cross-linked gels. The first is that a series of supposedly identical dry gel samples do not swell to the same extent in pure solvent. The variations encountered are greater the smaller the amount of cross-linking agent present. As one example, 20 identical samples containing 0.033 percent divinylbenzene showed equilibrium weight swelling ratios in toluene ranging from 19.15 to 20.98 times the dry weight, with an average value of 20.43. The second difficulty is that these gels contain an appreciable amount of soluble polymer which



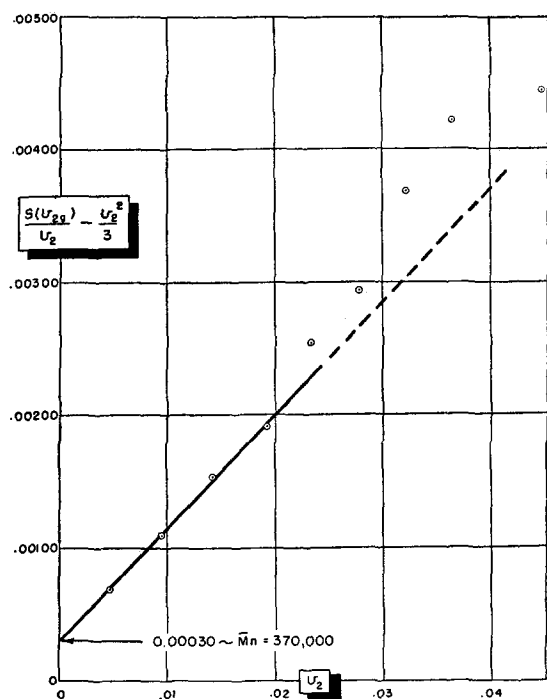


FIG. 6. Application of Eq. (9) to the deswelling of 0.033 percent divinylbenzene-styrene copolymer gels by toluene solutions of polystyrene having an osmotic pressure molecular weight of 300,000.

leaches out with time. Staudinger has already noted this fact, pointing out that the amount of soluble material increases with decreasing divinylbenzene content.<sup>8</sup> In some cases 50 to 60 percent of soluble polymer was recorded. An obvious expedient has been to start with a large number of samples, leave them in toluene until the weight has passed through a maximum and then decreased to a constant value, and finally to choose from this group the few needed samples which are reasonably close together in swelling ratio. Several changes of solvent are required so that the soluble polymer will not influence the swelling ratio. Only then should the gels be transferred to high polymer solutions for deswelling observations.

Table I presents some deswelling data obtained on gels that were so treated. Out of 20 original samples it was not possible to find the required 10 whose stabilized weights were sufficiently close. Three groups of samples, each with an appropriate blank, were finally transferred to toluene solutions of polystyrene. Column 2 lists the maximum weight swelling exhibited by these

gels in pure solvent, while column 3 is the stabilized weight ratio after most of the soluble polymer had been removed by toluene.  $v_2$  is the volume fraction of polystyrene in solution, after correction for dilution by the toluene which left the gels during deswelling.  $v_{2g}$  is the volume fraction of polymer in the deswollen gels. In calculating  $v_{2g}$  it was assumed that the original sample weight had decreased by 10 percent through loss of soluble material. This is admittedly a crude approximation based on the fact that the stabilized weight ratios are about 10 percent less than the maximum weight ratios, and on the assumption that the soluble polymer while still in the gel was swollen approximately 20 times. A more exact treatment for the effect of soluble polymer is evidently needed. The remaining columns of the table show the calculated quantities needed to compute a molecular weight.  $\mu_g$  was again assumed to be 0.44, while the density of the dry gel was taken as 1.05. Figure 6 is a plot of this data according to Eq. (9). The extrapolated value for  $1/\bar{x}_n$  is 0.00030, thus indicating a number average molecular weight of 370,000 for the polystyrene. Osmotic pressure measurements in methyl *n*-amyl ketone gave a molecular weight of 300,000 for this same polymer, while light scattering measurements indicated 302,000. From the slope of the line,

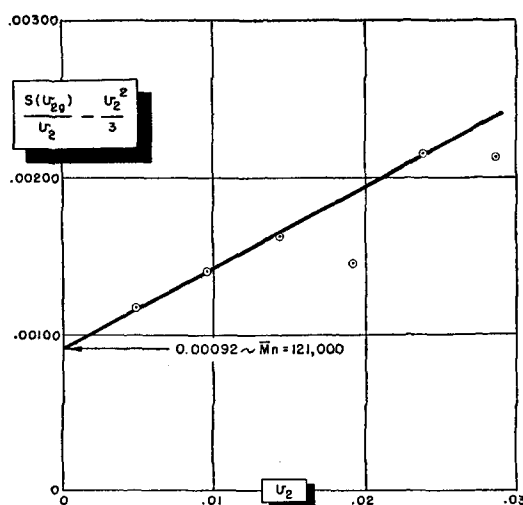


FIG. 7. Application of Eq. (9) to the deswelling of 0.0462 percent divinylbenzene-styrene copolymer gels by toluene solutions of polystyrene having a molecular weight of 115,000 by light scattering.

$\mu_1$  is 0.42. This is lower than the value of 0.44 given by Huggins,<sup>7</sup> or the several values listed by Mark.<sup>9</sup> This particular polystyrene had been prepared in mass without catalyst at 100°C.

The first four points of Fig. 6 lie exactly on a straight line, while the points for more concentrated solutions depart from this line in a way which suggests an upward curvature. Similar curvature in osmotic pressure curves has been observed.<sup>9,22</sup> The points which are off the curve had different swelling ratios in pure solvent than the first four points, as can be seen in the table. In one other example, shown in Fig. 7, toluene solutions of a polystyrene prepared by emulsion polymerization at 80°C were used to deswell a series of gels containing 0.0462 percent divinylbenzene. The number average molecular weight from the deswelling data was 121,000, compared with a light scattering molecular weight of 115,000.  $\mu_1$  came out as 0.45. These gels swelled in toluene to approximately 12 times their dry weight, and contained less soluble matter than the 0.033 percent gels. In both cases uncertainty exists because of our assumption that  $\mu_g = 0.44$ , and because of soluble constituents in the gels. In general these two sets of measurements appear to confirm the theory. However, a series of narrow polymer fractions of known molecular weight should be measured on one series of gels, and cross-checked on gels of different swelling power, and with different solvents before the general validity of the method can be assessed.

#### DISCUSSION OF THE METHOD

Because of limited experience, it is obviously impossible at the present time to offer a critical evaluation of this gel method of measuring molecular weights of high polymers. There are, however, some general considerations which might be discussed for and against the method.

1. The simplicity of the method is its most striking feature. It is possible to have dozens of gels available for use at any time.

2. The accuracy in measurement characteristic of any method employing an analytical balance is potentially available here. Julander and Svedberg<sup>23</sup> have already shown that the

accuracy of osmotic pressure measurements can be increased tenfold by use of a weighing technique. Some osmotic pressure methods involve an uncertainty of 10 percent for  $\bar{M}_n$  of 70,000 which increases to 50 percent at  $\bar{M}_n = 225,000$ .<sup>24</sup> More precise results have been obtained.<sup>25</sup> It is difficult to assign an uncertainty figure for the gel method, but at the present time it is likely no better than osmotic pressure techniques.

3. These gels can probably be used at elevated temperatures to measure difficult soluble polymers. Polyethylene does not show much solubility below 70°C, while polyvinylidene chloride is usually studied by viscosity in *o*-dichlorobenzene at 120°C. The latter polymer in particular defies any existing method of absolute molecular weight determination. There is a possibility for depolymerization of the gel network at high temperature.

4. A long time is required for these gel samples to reach their equilibrium deswelling value. This can be off-set in part by having a large number of gels in use, so that the total data obtained over a given time will be appreciable.

5. Mildly cross-linked gels are not ideal in their behavior, as mentioned before. Variation in swelling ratio of identical gels, and loss of soluble constituents are the principle disadvantages. Some gel samples swell in peculiar fashion with small protuberances or depressions. Experience in preparing gels may show how to eliminate these faults. Divinylbenzene monomer is probably far from ideal because it polymerizes more readily than styrene, and may be totally consumed before completion of polymerization. This would lead to excessive soluble matter. A system like methyl methacrylate-glycol dimethacrylate may give a more homogeneous gel.

6. The numerical calculations involved in applying Eq. (9) are tedious although the work required can be lessened by the construction of special charts and tables. Eq. (8) is somewhat simpler to manipulate.

7. Finally, there is some question about the absolute accuracy of the thermodynamic theory of high polymer-solvent systems. Flory has been critical of the theory, pointing out that it holds

<sup>22</sup> M. L. Huggins, *Ind. Eng. Chem.* **35**, 980 (1943).

<sup>23</sup> I. Julander and T. Svedberg, *Nature* **153**, 523 (1944).

<sup>24</sup> R. H. Wagner, *Ind. Eng. Chem. Anal. Ed.* **16**, 520 (1944).

<sup>25</sup> P. J. Flory, *J. Am. Chem. Soc.* **65**, 372 (1943).

better for concentrated solutions than for the dilute solutions of interest here. He has attempted to correct this situation.<sup>26</sup> Flory has also emphasized that three-dimensional polymers are usually not perfect networks, but contain many loose chain ends which do not contribute their full share toward swelling equilibrium. He has indicated a method of correcting for this.<sup>27</sup> This same article contains a curve showing excellent correlation between swelling of vulcanized rubber samples in pure solvent, and the modulus of

elasticity of the dry gel at 300 percent elongation. Such data indicate that the Flory-Rehner theory of swelling is essentially correct.

#### ACKNOWLEDGMENT

I should like to express appreciation here to Dr. P. R. Wenck for several discussions on the biological aspects of osmotic pressure; to my wife for the detailed numerical calculations required for Figs. 1 through 5; to Dr. P. J. Flory for critical comments and valuable suggestions concerning the method; and to Dr. J. J. Grebe who has consistently encouraged interest in new methods of determining molecular weights and molecular weight distributions on high polymers.

<sup>26</sup> P. J. Flory, paper presented at the Pittsburgh meeting of the American Chemical Society, September, 1943. See also W. J. C. Orr, *Trans. Faraday Soc.* **40**, 320 (1944); T. Alfrey and P. Doty, *J. Chem. Phys.* **13**, 77 (1945).

<sup>27</sup> P. J. Flory, *Chem. Rev.* **35**, 73 (1944).

THE JOURNAL OF CHEMICAL PHYSICS VOLUME 13, NUMBER 9 SEPTEMBER, 1945

### The Adsorption of Gelatin to Silver Bromide\*

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(Received June 7, 1945)

Experimental data are presented illustrating a *specific case* of amphipathic adsorption, namely, of gelatin to silver bromide. In this there is mutual coagulation of the silver hydrosol and protein, followed by peptization in excess of dissolved protein. The phenomena in their relation to the isoelectric point of the protein and the pH of the solution are interpreted in terms of a basically duplex polar : non-polar structure in proteins, and of a resonance factor, involving both adsorbent and adsorbate, in similar cases.

**I**N previous work<sup>1</sup> it was observed that:

(i) At pH 6.5 and 50°C washing left a constant residual amount of gelatin on silver bromide grains from a photographic emulsion, in the specific case, about 3.4 mg per g. There was but slight change between pH 4 and pH 10.

(ii) By digesting with boiling water, the amount retained was reduced to about one-half.

(iii) From the photomicrographically determined grain size-frequency the surface area of the grains could be obtained. From this, and taking a value *ca.* 8A for the thickness of a monomolecular layer of gelatin, it could be concluded that the gelatin was held primarily in a monomolecular layer, with a secondary layer attached by weaker forces.

Subsequently, it was noticed<sup>2</sup> that Zsigmondy has recorded that gold foil dipped in gelatin solution retained a small amount of gelatin not removed by boiling water. Our more recent\*\* experiments have been carried out with silver bromide hydrosols, prepared with a slight excess of bromide ion. A standard sol was prepared, usually in a quantity of 4 liters, as follows: 200 ml of 0.40N AgNO<sub>3</sub> and 200 ml of 0.440N KBr were run simultaneously into 3600 ml of distilled water continuously stirred. The bromide

<sup>2</sup> R. Zsigmondy, translated by E. R. Spear, *The Chemistry of Colloids*, Part I (O. Spamer, Leipzig, 1912), p. 112. "As early as 1900 the author (R. Zsigmondy) demonstrated that gold foil adsorbed gelatin and covered itself with a layer that could not be removed by boiling water. This layer prevented the amalgamation of the gold with mercury."

\*\* This work has been repeatedly interrupted by pressure of war work.

\* Communication No. 1038 from the Kodak Research Laboratories.

<sup>1</sup> S. E. Sheppard, R. H. Lambert, and R. L. Keenan, *J. Phys. Chem.* **36**, 174 (1932).