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The Role of Matrix Mechanical Stress in Swelling Equilibrium and Transport through Networks

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ABSTRACT: It is shown that swelling equilibrium of a network space requires that the hydrostatic pressure inside the matrix be raised to compensate the change in solvent chemical potential induced by mixing with the network substance. This pressure rise, over ambient, is due to an extra stress in the matrix substance which balances it mechanically. The transport equation for flow through the matrix was expressed with the network (matrix) force balance equation considered specifically. The role of the network substance chemical potential gradient in the transport was elucidated. The distribution of the network substance pressure and stress was considered for the case of one-dimensional gradients driving steady-state flow. Use was made of specific friction coefficients to describe the transport coefficients.

A system in internal thermodynamic equilibrium is defined by the nature of its confining walls and the force determining potentials at which they are placed. If the walls have isolating properties then the system is totally out of contact with its environment. Any potential which is applied from outside will not disturb the system. The potentials most commonly in question are the temperature, the mechanical stress, and the chemical potential. If the walls are thermally insulating, any outside temperature can prevail; if they are rigid, any outside stress may be applied; if they are impervious, any environment of any composition and any level of chemical potential can be placed outside. If on the contrary the system is open, i.e., if all externally existing potentials are transmitted, equilibrium in the system will only then occur if and when the system potentials are uniformly the same throughout and match the values of these potentials as they exist uniformly on the system's boundary. If this is not the case and the potentials, over the system's boundary, are not the same, gradients will arise within the system to bridge the imposed potentials. Along these gradients transport will then occur: of heat (entropy), if there is a temperature gradient; of volume, if there is a stress gradient; and of chemical species, if there is a chemical potential gradient.

For present purposes we will assume that no temperature gradient arises and that the system is isothermal. The condition of stability, of whether flow will or will not arise, then depends upon the distribution of the mechanical and chemical forces which are imposed. The question both of mechanical and of chemical equilibrium has to be considered.

This rather obvious point may in many instances be ignored. In mechanics one commonly deals with uniform one-component bodies and no problem of chemical equilibrium arises. In thermodynamics, on the other hand, study objects often are gases or liquids and only a uniform hydrostatic pressure can prevail. The neglect, therefore, of chemical equilibrium in mechanics and of mechanical equilibrium in chemical thermodynamics is often justified, but must not be forgotten. It is fatal if it becomes a habit and involves the uncritical extension of this practice to all cases. In particular for systems possessing solid or semisolid character, where a more complex stress pattern than just a hydrostatic pressure can and must in general arise, the question of mechanical equilibrium of each and every part of the system has to be explicitly considered and assigned equal status to the question of chemical stability.

In this paper we are concerned with one class of system only, with gels, i.e., with fluid filled porous solid structures where the gel substance, the porous support, is chemically a component of the system but mechanically possesses solid-like properties. We wish to consider such systems both from the point of view of their internal equilibrium and of their use to achieve separation or filtration flow.

We will first discuss the question as it arises in membrane equilibrium by establishing the connection between the membrane and a swollen gel. We will show in particular that the membrane is an "engine" which can convert chemical energy into mechanical energy and that "osmotic pressure" should be seen as the output of such an engine. We will then pass from equilibrium to the steady state, from balanced potentials across the gel (the membrane) to unbalanced ones involving the flow of one and then two components through the gel matrix.

This will involve us in the discussion of two aspects, the nature of the driving forces and the nature of the functional resistance met in flow. In particular the role of a gel substance, chemical potential gradient involving a mechanical stress pattern in the gel substance, will be considered, admittedly in the simplified situation where the flows and gradients in the stress and other involved potentials occur in one dimension only.

Membrane Equilibrium

The chemical potential of a species changes when it is mixed with another species, or when its state of stress is altered. Specifically, if species 1 is, say, a liquid and another species, the solute 2, is dissolved in it, the chemical potential of species 1 will be lowered. If an extra pressure is applied the chemical potential will be raised. If both are done simultaneously the two effects can be made to cancel and the chemical potential of species 1 in the solution at the higher pressure can be made to equal the chemical potential of species 1 in a pure phase at the reference pressure. Suitably contacted, the two phases are in osmotic equilibrium, i.e., equilibrium with respect to solvent.

One way to demonstrate osmotic equilibrium is to bring the two phases together through a membrane permeable only to species 1 (Figure 1). A semipermeable membrane is a very clever device which has to achieve two purposes simultaneously. It must be species selective; it must, say, have holes just big enough so that molecules of the solvent (species 1), but not of the solute (species 2), can cross. It must be supportive of mechanical stresses and its mechanical properties must be adequate so that it can develop forces to balance the required pressure difference. Both properties are essential. If the holes are too big, the solute will distribute between the two phases; if the elastic modulus and the strength of the membrane are not big enough, the required pressure difference could not be generated.

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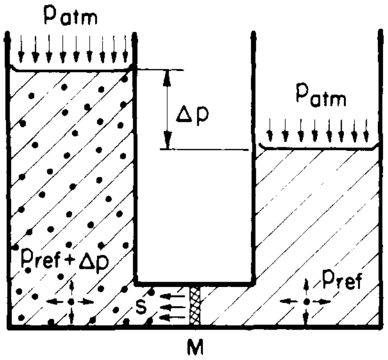

Figure 1. The semipermeable membrane in thermodynamic equilibrium. The solvent (species 1) is on both sides of the membrane M; the solute (species 2) exists only in the left-hand compartment. The chemical potential of the solvent, eq 20, at equilibrium corresponds to $\Delta p = -(kT/\bar{V}_1) \ln a_1$, where a_1 is the activity of species 1 on the left and s is the extra stress in the membrane.

Equilibrium Swelling of Gels

The solute in Figure 1 was not specified. Let it for the moment be a macromolecular species involving freely coiling chains of equal size. If we now take these macromolecules and tie their ends together, a few at a time, we generate a macroscopic three-dimensional network which will still be miscible with species 1, i.e., will tend to imbibe the solvent, when exposed to it. It will, in fact, swell to form a gel. Swelling is not unlimited and will stop when equilibrium with respect to solvent chemical potential has been reached. This will occur long before the chains are fully extended. As a result, the chains in the equilibrium state are still capable of considerable conformational rearrangement and although their conformational freedom is much reduced, as compared with the free solution, the entropy and corresponding free energy change are finite and can be calculated. It is then customary[1] to add the free energy change due to mechanical expansion (from a reference state) to the energy change due to network dilution and minimize the sum with respect to the expansion coefficient. Since this involves only one operation, the expulsion, or imbibition, of pure solvent, the minimization of the free energy with respect to expansion really represents its differentiation with respect to solvent content, i.e., to the derivation of the chemical potential of the solvent and its equalization with the chemical potential of the pure solvent species with which it is in contact. Swelling equilibrium, just as osmotic equilibrium, thus implies a balance of chemical potential of the solvent in the gel and outside of it (Figure 2). No semipermeable membrane is required in this case since the solute particles are all linked together.

Does the absence of such a membrane, however, imply also the absence of a pressure difference between the two phases. In general, this point is not addressed, and while the free energy of expansion of the network from its reference configuration is correctly considered to be a change in the standard free energy of the network component, any mechanical consequences of this are either totally ignored or considered to be incidental. Quite the contrary is true. A pressure rise is called for in order to balance solvent chemical potential, just as in osmotic equilibrium. The only difference is that in this case the tension developed in the network, by swelling, is the device the system uses to create the higher pressure. The pressure difference between the two sides of the surface of a swollen gel is thus compensated mechanically, or more correctly created, by the tension in the network strands.

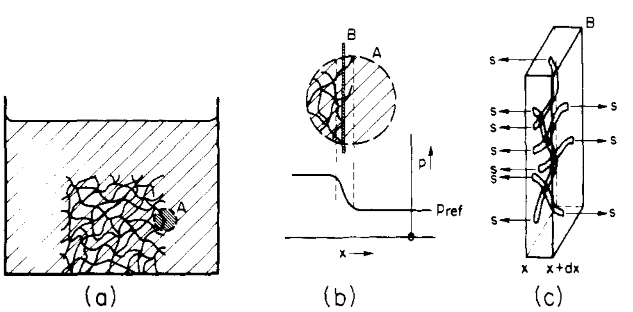

Figure 2. Equilibrium swelling of a gel. (a) Cross-linked gel network (species 3) in a container of pure solvent (species 1). (b) Region A in (a) enlarged. The concentration $c_3(x)$ of gel substance segments decreases as we go from the homogeneous interior of the swollen gel to pure solvent outside. In parallel, the pressure $p(x)$ drops from its value to the reference pressure p_{ref} in the pure solvent. (c) Region B in (b) enlarged. Each network strand carries the extra stress $s(x)$ per unit volume. The stress s is the same per strand on the average and is taken to be positive if it points outwards over the surface of the lamella which the two planes at x and $x + dx$ define. If both the concentration and the pressure vary we have, for mechanical force balance in the x direction: $(dp/dx) = (dc_3\bar{V}_3 s/dx)$.

Both positive and negative pressure differences can be induced depending upon the outside conditions. What is important is to realize that it is this change in pressure in the solvent, in addition to network segment concentration changes, which affects solvent chemical potential and that it is the stress in the network (tension or compression) which creates this pressure and thus maintains both mechanical and solvent chemical potential balance.

In going through the surface there is no abrupt change in the pressure much as there is no abrupt change in the network segment concentration from zero outside to its mean value in the bulk. In fact, these two functions are interrelated as Figure 2b shows. A gradient in network segment concentration c_3 is accompanied by a pressure gradient such that the pressure change compensates not only the stress in the network per unit cross section, but also the change in solvent activity which accompanies a change in c_3. Quite in general, whenever there is a gradient of concentration of polymer segments as, say, between a gel swollen to equilibrium and the surrounding solvent, there is a gradient in pressure which compensates for the gradient in the number of stress-carrying chains that cut across an arbitrary cross section. We have the situation of Figure 2c. Let us consider the mechanical equilibrium of a slab of the system dx thick and of unit cross section. For mechanical balance we have

$$sc_3\bar{V}_3(x) - p(x) = sc_3\bar{V}_3(x) + [(d(sc_3\bar{V}_3)/dx)\, dx] - p(x) - [(dp/dx)\, dx]$$

where p is the pressure, s is the average extra stress per unit volume of the severed strand, c_3 is the concentration of strands crossing the interface at x, and $\bar{V}_3$ is the molecular volume per strand. Hence

$$d(sc_3\bar{V}_3)/dx = dp/dx \qquad (1)$$

so that the pressure at a point x inside a gel, where its concentration is c_3, is given by

$$p = p_{ref} + \int_0^x [d(sc_3\bar{V}_3)/dx]\, dx = p_{ref} + sc_3\bar{V}_3 \qquad (2)$$

The pressure p_{ref} is the pressure at the point $x = 0$ assumed to be located somewhere in the pure solvent phase.

It should be emphasized, moreover, that p is the pressure not only in the solvent but also in the network. The stress s represents an additional stress in the network material over and above the isotropic pressure. Moreover, since the network constitutes a component of the system thermodynamically the chemical potential of this species is changed by the change in pressure p, by the change in the stress s, and by the change in concentration c_3. The change in network activity a_3 is linked to the change in solvent activity a_1 by the Gibbs–Duhem relation.

In Figure 2c and in the discussion till now we have implicitly assumed that the gradients of p, s, and c_3 are in the x direction and are independent of y and z. The interface is thus plane. If, as is more generally the case, the membrane is curved there are additional components of the stress in the network to be averaged in the x direction much as in the case of interfacial tension. Hence, in addition to the effect on p of network segment concentration and stress variations in the x direction, network conformational deformations, in other than the x direction, have to be considered. In fact how much of each occurs, by how much c_3, s, and deformation varies in the interface and in the bulk, is determined by the overall free energy minimum under the geometric constraints imposed on the gel by its macroscopic shape and confinement. In this discussion we will treat only the case of the plane interface which is assumed to remain plane under all circumstances considered here.

Transport through Gels

If the gel network is attached to some suitable rigid support this can be used to compensate a pressure difference which may be applied across it. Relative transport could then occur giving rise to frictional forces. Any out of balance force would change s and be compensated by forces supplied by the rigid frame.

The semipermeable membrane in Figure 1 could in practice be a swollen gel which is attached to the rigid framework of the "osmometer". Interface deformation and curvature would almost certainly arise in this case, but are neglected by assumption. Figure 3 is an "expanded" schematic view of the membrane region of Figure 1. In Figure 3a both sides of the membrane are in contact with pure solvent. In Figure 3b, we have a solution of larger, fully retained solute particles on the left-hand side, as in Figure 1.

For equilibrium (no transport) the stresses compensate mechanically and the chemical potential of solvent everywhere equals that of pure solvent 1 at temperature T and pressure p_{ref}. This is trivially true for the two pure solvent phases. Inside the membrane, however, the effect of the membrane component is to influence solvent activity a_1, but the change induced is exactly balanced by the pressure rise Δp. Moreover, since a change in solvent activity a_1 requires there to be a change in network activity a_3 (by the Gibbs–Duhem relation)

$$c_1 \, \mathrm{d} \ln a_1 + c_3 \, \mathrm{d} \ln a_3 = 0 \qquad (3)$$

The network substance concentration c_3 is changed, giving rise to the force $sc_3\bar{V}_3$ which produces the required Δp.

We now turn to the situation of Figure 3b. We again assume equilibrium and since the right-hand face continues to be in equilibrium with pure solvent its situation will be the same as in Figure 3a. On the left-hand side, however, the solvent chemical potential must be compensated under different conditions. Due to the finite concentration of impenetrable solute 2 the solvent activity is a_1^{soln} and not 1 and a pressure Δp^{soln} is developed to counterbalance this. Both the stress s and the pressure p in the membrane will thus have to be higher at its left-hand face and the concentration of membrane segments $c_3(x)$ too will differ from its value on the right. It is recalled that mechanically, the increased pressure in the gel is compensated by an increase in $s\bar{V}_3c_3$ where both s and c_3 will change in general. Only if the network were rigid would c_3 be constant and only s would change. With compliant gels the mechanical equation of state and the geometry of the attachment determine how s and c_3 vary.

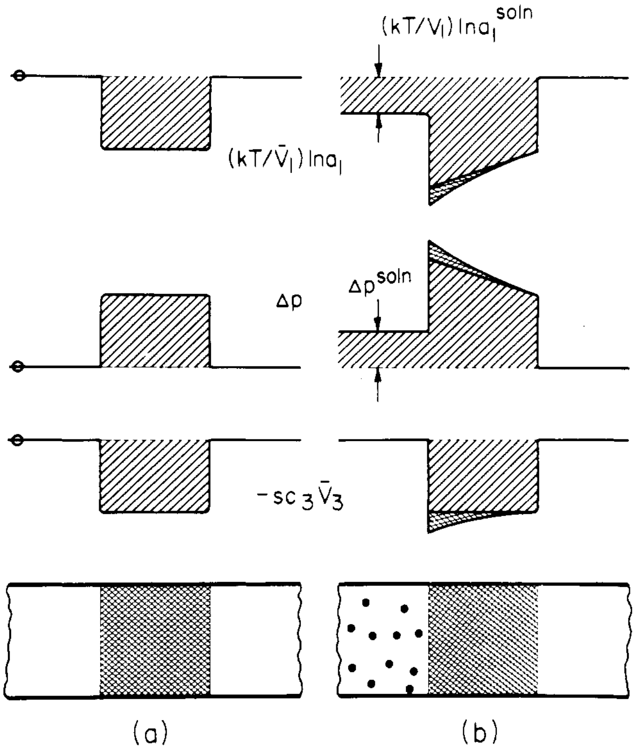

Figure 3. Conditions inside a semipermeable membrane in equilibrium (region M of Figure 1 enlarged). (a) Pure solvent to either side of the membrane: Due to the finite concentration c_3 inside the membrane, the activity of the membrane substance $a_3 \neq 1$ and by the Gibbs–Duhem relation $a_1 \neq 1$. Hence, while $a_1 = 1$ and $(kT/\bar{V}_1) \ln a_1$ is zero outside the membrane it is negative inside. To achieve solvent chemical potential balance with the outside the pressure inside the membrane has to rise by $\Delta p = -(kT)/\bar{V}_1) \ln a_1$. To build up such a pressure difference the network will have to develop a stress s per unit volume in the x direction within it (s is defined as positive for tension). Hence $\Delta p = sc_3\bar{V}_3$. The rigid support in which the membrane is placed compensates for unbalanced stresses in all other directions. No membrane "bulging" is assumed. (b) Pure solvent to the right of the membrane, a solution of an impermeant species 2 on the left: Due to the solute on the left-hand side the pressure there has to be raised by Δp^{soln} to compensate for the induced solvent activity change $(kT/\bar{V}_1) \ln a_1^{\text{soln}}$: $\Delta p^{\text{soln}} = -(kT/\bar{V}_1) \ln a_1^{\text{soln}}$. Hence the pressure in the membrane will be higher on the left-hand than on the right-hand side by Δp^{soln}. Correspondingly solvent activity inside the membrane will have to be lower on the left-hand than on the right-hand side. This must affect network substance activity a_3 and thus the network substance distribution c_3. Hence also $sc_3\bar{V}_3$ will be higher on the left-hand than on the right-hand side. The light shaded region shows the changes in a_1 and p to be expected when c_3 remains constant. The dark shaded additions indicate the effect of a variation in c_3.

It is to be reiterated that no bulging of the gel system is assumed to occur. In this way the lateral tensions in the gel do not contribute, via the Laplace equation, to the pressure difference Δp^{soln}.

Despite the pressure gradient across the membrane, in Figure 3b there is no gradient of solvent chemical potential in equilibrium and no flow. If conditions on either side of the membrane are suddenly changed, however, this will no longer be true and a flow of solvent will occur and persist as long as there is a gradient in the chemical potential.

Semipermeable Membrane (Gel) in Steady-State Flow

At constant temperature the gradient in the solvent chemical potential depends upon p and a_1 and is given by

$$\nabla\mu_1 = \bar{V}_1\nabla p + kT\nabla \ln a_1 \tag{4}$$

where $\bar{V}_1$ is the molecular volume of solvent and it is assumed that the one-dimensional gradients in activity a_1 and pressure p are in the direction normal to the membrane surface.

We now write the equations of motion of a representative unit volume of solvent 1 and of gel network substance 3 normal to the face of the membrane[2,3,4]

$$X_1 + F_{13} = 0 \tag{5}$$

$$X_3 + F_{31} = 0 \tag{6}$$

In equations 5 and 6

$$F_{13} = -\hat{f}_{13}(v_1 - v_3) \tag{7}$$

$$F_{31} = -\hat{f}_{31}(v_3 - v_1) \tag{8}$$

The forces F_{13} and F_{31} are the frictional forces resulting from the motion of the solvent 1 and the network component 3 with velocities v_1 and v_3, respectively, relative to the points of attachment of the gel to the rigid support. The factors $\hat{f}_{ij}$ are friction factors giving the force per unit volume of component i per unit relative velocity of component i with respect to the combined motion of all of component j.[4] The $\hat{f}_{ij}$ are nonnegative quantities and should be distinguished from the molecular friction coefficients $f_i = \bar{V}_i\hat{f}_{ij}$.[3] The $\bar{V}_i$ are the molecular volumes.

The terms X_1 and X_3 are the driving forces per unit volume of components 1 and 3, respectively, and are related to their chemical potential gradients as follows:

$$X_1 = -\nabla\mu_1/\bar{V}_1 \tag{9}$$

$$X_3 = -\nabla\mu_3/\bar{V}_3 \tag{10}$$

In the steady state, the velocity v_3 of the network equals that of the rigid frame to which it is attached. We can put

$$v_3 = 0 \qquad \text{steady state} \tag{11}$$

without loss in generality. Hence for the steady state

$$F_{13} = -\hat{f}_{13}v_1 \tag{12}$$

$$F_{31} = \hat{f}_{31}v_1 \tag{13}$$

and substituting (12) and (13) into (5) and (6), respectively

$$(-\nabla)\mu_1/\bar{V}_1 - \hat{f}_{13}v_1 = 0 \tag{14}$$

$$(-\nabla)\mu_3/\bar{V}_3 + \hat{f}_{31}v_1 = 0 \tag{15}$$

Multiplying eq 14 and 15 by $c_1\bar{V}_1$ and $c_3\bar{V}_3$ respectively and adding we find that, at each position x in the membrane,

$$c_1(-\nabla)\mu_1 - c_1\bar{V}_1\hat{f}_{13}v_1 + c_3(-\nabla)\mu_3 + c_3\bar{V}_3\hat{f}_{31}v_1 = 0 \tag{16}$$

Since each lamellar region at x is in equilibrium, the Gibbs–Duhem relationship

$$[-\mathrm{d}p + c_3\bar{V}_3\,\mathrm{d}s] + [\sum_i c_i\,\mathrm{d}\mu_i] = 0 \tag{17}$$

can be applied and combining eq 1, 16, and 17 we obtain

$$c_1\bar{V}_1\hat{f}_{13} = c_3\bar{V}_3\hat{f}_{31} \tag{18}$$

which is a particular case of a general relationship (Onsager principle)[2-4] which links the friction factors $\hat{f}_{ij}$ and $\hat{f}_{ji}$:

$$c_i\bar{V}_i\hat{f}_{ij} = c_j\bar{V}_j\hat{f}_{ji} \tag{19}$$

Even in the trivial case of transport of pure solvent through the membrane, the need to treat the gel substance as a component is thus demonstrated. Since

$$\mu_1 = \mu_{10} + \bar{V}_1\Delta p + kT\ln a_1 \tag{20}$$

and

$$\mu_3 = \mu_{30} + \bar{V}_3\Delta p - \bar{V}_3 s + kT\ln a_3 \tag{21}$$

where μ_{10} and μ_{30} are standard chemical potentials at p_{ref} and T and s is the extra stress per unit volume of the gel substance, we can substitute eq 18, 20, and 21 into eq 14 and 15 and immediately derive the equation of mechanical balance in the membrane

$$(-\nabla p) - (-\nabla c_3\bar{V}_3 s) = 0 \tag{22}$$

In arriving at the above result use was made of the fact that $c_i\bar{V}_i$ is the volume fraction of component i and that

$$\sum_i c_i\bar{V}_i = 1 \qquad i = 1, 2, 3 \tag{23}$$

It will be noticed that the Gibbs–Duhem eq 17 includes, as it should, the change in mechanical work (due to changes in the intensive variables p and s) $[-\mathrm{d}p + c_3\bar{V}_3\,\mathrm{d}s]$ per unit volume of the system as it exists in local equilibrium between x and $x + \mathrm{d}x$. Mechanical equilibrium, however, as expressed by eq 1, tells us that this term is zero. Hence we could conclude that $\sum_i c_i\,\mathrm{d}\mu_i = 0$ and that the Onsager reciprocal relation (eq 18) has to hold. The derivation of eq 22 goes the opposite way. Both the Gibbs–Duhem relation and the Onsager principle are assumed to apply and give the result of eq 22 as a consequence of the equations of motion, eq 14 and 15.

Substituting the expression for the gradient of solvent chemical potential, eq 4, into eq 14 gives

$$v_1 = (1/\hat{f}_{13})[(-\nabla p) + (kT/\bar{V}_1)(-\nabla)\ln a_1] \tag{24}$$

Equation 24, like all the above equations, is a local equation and the gradients and the coefficients are characteristic of the condition prevailing at that point. If eq 24 is averaged over the membrane, J remains the same, $(-\nabla p)$ becomes $(-\Delta p/\Delta x)$, the difference in pressure divided by the thickness, and $(-\nabla)\ln a_1$ averages to zero. Instead of $\hat{f}_{13}$, however, we must write $\langle\hat{f}_{13}\rangle$, the average value of the friction coefficient, and eq 24 then becomes Darcy's law[5]

$$J = (K_s/\eta_1)(-\Delta p/\Delta x) \tag{25}$$

where $J = c_1\bar{V}_1v_1$ is the flux across the membrane, Δx is its thickness, η_1 is the solvent viscosity, and K_s is the permeability. Hence,

$$K_s/\eta_1 = (c_1\bar{V}_1)/\langle\hat{f}_{13}\rangle \tag{26}$$

and K_s can be used to determine $\langle\hat{f}_{13}\rangle$.[4]

The system of Figure 3b involves three components if the rigid container walls are ignored. The way the system is arranged, however, there are never more than two components in any one phase and thus a simple two-component description could be applied to the gel even in the case of Figure 3b.

The system becomes more complex if the solute species 2 can penetrate the gel space.

Steady-State Flow of a Solution through a Gel

We will now treat the nonequilibrium thermodynamics of permeation of a solution through a gel in the light of our above discussion. We shall treat a three-component case, where the solvent 1 contains a diffusible solute species 2 which can enter the gel space but will move through it at a velocity different to that of the solvent. This is the simplest case which displays the features of component separation.

The steady-state equations of motions instead of eq 5 and 6 become

$$X_1 + F_{12} + F_{13} = 0 \tag{27}$$

$$X_2 + F_{21} + F_{23} = 0 \tag{28}$$

$$X_3 + F_{31} + F_{32} = 0 \tag{29}$$

where, as before,

$$F_{ij} = -\hat{f}_{ij}(\upsilon_i - \upsilon_j) \qquad i, j = 1, 2, 3 \tag{30}$$

$$X_i = -\nabla\mu_i/\bar{V}_i \qquad i = 1, 2, 3 \tag{31}$$

The step from eq 5 and 6 to eq 27–29 is actually further reaching than it may seem. Let us consider eq 15 and 27, for example. Whereas the force F_{13} in eq 5 is the total friction $F_{1,\mathrm{total}}$ experienced by a unit volume of species 1 in its movement past species 3, the force F_{13} in eq 27 is only part of this resistance. It is in fact not generally true that the total resistance in this case can be split additively into the two parts F_{12} and F_{13} defined by eq 30. It is, however, reasonable to expect that the approximation

$$F_{1,\mathrm{total}} = F_{12} + F_{13}$$

is an expansion of $F_{1,\mathrm{total}}$, up to the linear terms, in the variables $\upsilon_1 - \upsilon_2$ and $\upsilon_1 - \upsilon_3$.

Actually only two of eq 27, 28, and 29 are independent. This can be shown by multiplying them by $c_1\bar{V}_1$, $c_2\bar{V}_2$, and $c_3\bar{V}_3$, respectively, and adding. The sum is identically zero when use is made of eq 17 and 19. Hence, of the three unknown velocities υ_1, υ_2, and υ_3, only two are independent. In fact it is meaningless to try and solve for velocities absolutely. Only $(\upsilon_1 - \upsilon_3)$ and $(\upsilon_2 - \upsilon_3)$, say, are of interest and there is no loss of generality if as before we put $\upsilon_3 = 0$. We thus have

$$\upsilon_1 - \upsilon_3 = \upsilon_1 = (-\nabla\mu_1/\bar{V}_1\Lambda)(\hat{f}_{21} + \hat{f}_{23}) + (-\nabla\mu_2/\bar{V}_2\Lambda)(\hat{f}_{12}) \tag{32}$$

$$\upsilon_2 - \upsilon_3 = \upsilon_2 = (-\nabla\mu_1/\bar{V}_1\Lambda)(\hat{f}_{21}) + (-\nabla\mu_2/\bar{V}_2\Lambda)(\hat{f}_{12} + \hat{f}_{13}) \tag{33}$$

where

$$\Lambda = \hat{f}_{12}\hat{f}_{23} + \hat{f}_{13}\hat{f}_{21} + \hat{f}_{13}\hat{f}_{23} \tag{34}$$

In terms of these fluxes and forces the entropy production per unit volume is given by

$$\Phi = \sum c_i\upsilon_iX_i = c_1\upsilon_1X_1 + c_2\upsilon_2X_2 \tag{35}$$

Phenomenologically, it is preferable to define and use the volume flow[3]

$$J_\mathrm{V} = c_1\bar{V}_1\upsilon_1 + c_2\bar{V}_2\upsilon_2 \tag{36}$$

the separation flow

$$J_\mathrm{D} = c_1\bar{V}_1(\upsilon_2 - \upsilon_1) \tag{37}$$

and the conjugate forces X_V and X_D. Expressions for X_V and X_D are found by equating the coefficients of υ_1 and υ_2 after substituting for X_1, X_2, J_V, and J_D in

$$\Phi = c_1\upsilon_1X_1 + c_2\upsilon_2X_2 = J_\mathrm{V}X_\mathrm{V} + J_\mathrm{D}X_\mathrm{D} \tag{38}$$

One obtains

$$X_\mathrm{V} = (-\nabla p) - [c_1\bar{V}_1/(c_1\bar{V}_1 + c_2\bar{V}_2)](-\nabla\Pi_3) \tag{39}$$

$$X_\mathrm{D} = (-\nabla\Pi_2) + [c_2\bar{V}_2/(c_1\bar{V}_1 + c_2\bar{V}_2)](-\nabla\Pi_3) \tag{40}$$

where

$$(-\nabla\Pi_2) = (c_2/c_1\bar{V}_1)kT(-\nabla)\ \ln a_2 \tag{41}$$

$$(-\nabla\Pi_3) = (c_3/c_1\bar{V}_1)kT(-\nabla)\ \ln a_3 \tag{42}$$

and where use was made of eq 17 so that[6,7]

$$(kT/\bar{V}_1)(-\nabla)\ \ln a_1 = -(-\nabla\Pi_2) - (-\nabla\Pi_3) \tag{43}$$

In the absence of a gradient in gel substance activity, i.e., when $\nabla\Pi_3 = 0$, but only then, the forces X_V and X_D reduce to $(-\nabla p)$ and $(-\nabla\Pi_2)$, respectively.[3]

We may also write

$$J_\mathrm{V} = L_\mathrm{p}(X_\mathrm{V} - \sigma X_\mathrm{D}) \tag{44}$$

$$J_\mathrm{D} = L_\mathrm{p}(-\sigma X_\mathrm{V} + (\sigma + \eta(1 - \sigma))X_\mathrm{D}) \tag{45}$$

where

$$L_\mathrm{p} = [c_1\bar{V}_1(\hat{f}_{23} + \hat{f}_{12} + \hat{f}_{21}) + c_2\bar{V}_2(\hat{f}_{13} + \hat{f}_{12} + \hat{f}_{21})]/\Lambda \tag{46}$$

is the hydraulic permeability coefficient,

$$\sigma = c_1\bar{V}_1(\hat{f}_{23} - \hat{f}_{13})/[c_1\bar{V}_1(\hat{f}_{23} + \hat{f}_{12} + \hat{f}_{21}) + c_2\bar{V}_2(\hat{f}_{13} + \hat{f}_{12} + \hat{f}_{21})] \tag{47}$$

is the reflection coefficient, and η is a nonnegative new parameter[5] given by

$$\eta = c_1\bar{V}_1\hat{f}_{13}/c_2\bar{V}_2(\hat{f}_{13} + \hat{f}_{12} + \hat{f}_{21}) \tag{48}$$

The parameters L_p, σ, and η are the three independent transport coefficients. Equations 46, 47, and 48 express them in terms of three mechanistically more transparent, nonnegative, specific friction coefficients $\hat{f}_{23}$, $\hat{f}_{13}$, and $\hat{f}_{21}$. (The coefficient $\hat{f}_{12}$ which also appears is equal to $\hat{f}_{21}c_2\bar{V}_2/c_1\bar{V}_1$.) Note that these coefficients and these new representations are conjugate to the forces X_V and X_D in their expanded concept which includes the membrane substance as a stress-bearing chemically active component.

Of interest also are the fluxes J_{23} and J_{13} of solute 2 and solvent 1 relative to the gel substance. We find from eq 36 and 37 by using eq 31, 44, and 45 that

$$J_{23} = c_2\bar{V}_2\upsilon_2 = L_\mathrm{p}(1 - \sigma)[X_\mathrm{V} + \eta X_\mathrm{D}][c_2\bar{V}_2/(c_1\bar{V}_1 + c_2\bar{V}_2)] \tag{49}$$

and that

$$J_{13} = c_1\bar{V}_1\upsilon_1 = L_\mathrm{p}[X_\mathrm{V}(1 + \sigma c_2\bar{V}_2/c_1\bar{V}_1) - X_\mathrm{D}[\sigma + (\sigma + \eta(1 - \sigma))(c_2\bar{V}_2/c_1\bar{V}_1)]][c_1\bar{V}_1/(c_1\bar{V}_1 + c_2\bar{V}_2)] \tag{50}$$

Two special cases will now be investigated in these terms: When $\sigma = 1$ the solute 2 is totally excluded from the gel and substituting into eq 44, 45, 49, and 50 we find

$$J_\mathrm{V} + J_\mathrm{D} = 0 \qquad J_{23} = 0 \qquad J_{13} = L_\mathrm{p}(X_\mathrm{V} - X_\mathrm{D}) \qquad \sigma = 1 \tag{51}$$

i.e., $\upsilon_2 = 0$ as expected. The flux $J_\mathrm{V} = J_{13}$ in this case reduces to eq 24.

When $\sigma = 0$ the gel network does not mechanically distinguish between solvent 1 and solute 2, i.e., the coupling with the network is the same. We have

$$\hat{f}_{13} = \hat{f}_{23} \qquad \sigma = 0$$

and find (for $\sigma = 0$)

$$J_\mathrm{V} = L_\mathrm{p}X_\mathrm{V}$$

$$J_\mathrm{D} = \eta L_\mathrm{p}X_\mathrm{D}$$

$$J_{23} = L_\mathrm{p}[X_\mathrm{V} + \eta X_\mathrm{D}][c_2\bar{V}_2/(c_1\bar{V}_1 + c_2\bar{V}_2)]$$

$$J_{13} = L_\mathrm{p}[X_\mathrm{V} - \eta(c_2\bar{V}_2/c_1\bar{V}_1)X_\mathrm{D}][c_1\bar{V}_1/(c_1\bar{V}_1 + c_2\bar{V}_2)] \tag{52}$$

with

$$L_\mathrm{p} = (c_1\bar{V}_1 + c_2\bar{V}_2)/\hat{f}_{23} \qquad \sigma = 0 \tag{53}$$

$$\eta = c_1\bar{V}_1\hat{f}_{23}/c_2\bar{V}_2(\hat{f}_{23} + \hat{f}_{12} + \hat{f}_{21}) \qquad \sigma = 0 \tag{54}$$

Forces X_V and X_D

As eq 39 and 40 show, the forces X_V and X_D, conjugate to the flows J_V and J_D, respectively, reduce to the pressure and solute concentration gradients when $(-\nabla\Pi_3) = 0$, i.e., when the chemical potential of the gel network evidences no gradient in its concentration dependence. The absence of such a gradient has been assumed a priori in previous analyses[3,7] and the terms in $(-\nabla\Pi_3)$ which appear in eq 39 and 40 have thus been neglected. Altogether, the role of the network substance chemical potential gradient in affecting the transport through the matrix has not been sufficiently emphasized. Partly, this is due to the fact that the discussion tended to center on across membrane potential differences. All the above equations are local and both the coefficients and the forces may vary from point to point.

If eq 21, 22, 41, and 42 are used in eq 39 and 40 it can be shown that

$$X_V = -[c_3\bar{V}_3/(c_1\bar{V}_1 + c_2\bar{V}_2)](-\nabla\mu_3/\bar{V}_3) \qquad (55)$$

$$X_D = [c_2\bar{V}_2/c_1\bar{V}_1][(-\nabla\mu_2/\bar{V}_2) + (c_3\bar{V}_3/(c_1\bar{V}_1 + c_2\bar{V}_2)) \times (-\nabla\mu_3/\bar{V}_3)] \qquad (56)$$

It thus appears that the force X_V is in fact the chemical potential gradient induced in the gel network. Similarly X_D depends not only on $(-\nabla\Pi_2)$ but more generally both on the gradient of solute chemical potential and on the gradient of network chemical potential. When $\sigma = 0$ and the gel network is unselective the volume flow J_V and the separation flow J_D are proportional to X_V and X_D, respectively (eq 52). This makes the link between X_V and $(-\nabla\mu_3)$ particularly obvious. We would indeed, in such a case, expect the network to "flow" along its gradient in a frame of reference moving with J_V. Substituting eq 21 and 22 into the condition $(-\nabla\mu_3) = 0$, we find

$$\begin{gathered}[c_1\bar{V}_1/(c_1\bar{V}_1 + c_2\bar{V}_2)](-\nabla\Pi_3) = c_3\bar{V}_3(-\nabla s) = (-\nabla p) \\ (-\nabla\mu_3) = 0\end{gathered} \qquad (57)$$

Discussion

With the transport equations expressed in terms of the nonnegative friction coefficients $\hat{f}_{ij}$ it is much easier to construct various cases and interpret them.[3,6] A detailed model is of course still required for each particular case and the $\hat{f}_{ij}$ must still be expressed in terms of structural, molecular parameters. This is also true for the mechanical balance eq 22. This, too, has to be linked, specifically, to gel structure and the proper boundary conditions over the gel surface must be known and structurally allowed for.

The main purpose of the above analysis was to assign to the immobilized component, the gel substance, its proper role both with respect to mechanical load carrying propensity and to participation, thermodynamically, in controlling flow through molecularly sized matrix spaces. There are real stresses induced in the matrix, stresses which provide the compensation for the real hydrostatic pressure changes in the gel. Moreover, not only the solution components, but also the gel substance, have a chemical potential inside the gel. Normally, it does not require compensation with outside phases and at equilibrium it is at a constant level. But in transport problems, this chemical potential, too, can display a gradient and codetermine the flow through the matrix. Even though it is permissible to treat the fluid component in a gel as a separate phase, its local equilibrium with the immobilized phase must still be taken into account. Cases can be conceived where the neglect of the gel substance can be justified, but the arbitrary extension of such a simplified treatment to all matrix transport problems may lead to misconceptions and serious errors.

The idea that the gel substance may have some role to play in all aspects where other system components contribute to the potentials has arisen in many earlier discussions.[8-10] The treatments have, however, at best been partial only and much controversy has been generated because of diverging results. The flux J_{23} (eq 49) of solute relative to the gel substance or the flux $(c_2\bar{V}_2/c_1\bar{V}_1)J_D$ (eq 45) of solute relative to solvent are seen to depend both on the force X_V and the force X_D. Even though we may choose to put $(-\nabla p) = 0$ (no outside applied pressure gradient), the resulting expressions still depend upon $(-\nabla\Pi_2)$ and $(-\nabla\Pi_3)$. It is necessary to assume that $(-\nabla\Pi_3) = 0$ before equations result where, as in Fick's law, the flux $J = D(-\nabla c)$ of the transported species depends upon its own concentration gradient only. Since in general it is unlikely that $(-\nabla\Pi_3) = 0$, comparison of diffusion coefficients obtained in matrices with diffusion constants in free solution will be misleading not only because the frictional terms in a matrix are different but also because the driving force cannot be properly estimated. Note, however, that when $X_V = (-\nabla\mu_3) = 0$ the solute velocity $v_2 = (v_2 - v_3) = (\hat{f}_{13}/\Lambda)(-\nabla\mu_2/\bar{V}_2)$.

One serious misconception resulting from a lack of proper appreciation of the gel substance as a component concerns osmotic pressure. Whereas in reality osmotic pressure is a property of the membrane, it is almost universally regarded as a characteristic of the solution. How wrong this is follows from the fact that one and the same solution can produce very different osmotic pressures depending upon what membrane is used and what is placed on its other side.

A membrane, a selective porous fluid filled matrix, is an engine. A solution can be put on one side and a solvent phase on the other and the membrane can be made to pump solvent. It is converting energy derived from chemical potentials into mechanical work, very much as a heat engine burns fuel to achieve this purpose or an electric motor converts electricity. One can rate the membrane both by its input characteristics, the concentrations of the solutions it handles, or by its output characteristics, the level of osmotic pressure to which it can pump the solvent out of the solution into a pure solvent phase. If it is truly permselective and capable of storing the generated pressure difference, there will be no energy loss. If, however, solute leaks or if the induced stress relaxes because the gel network substance is viscoelastic, energy will be dissipated. Not only selectivity but the mechanical properties are essential. As a result, the conditions inside the device, which is usually a solid-like molecular sieve of some kind, are most interesting and worthy of careful consideration both in equilibrium and in the steady transport case.

For equilibrium the case of two diffusible components (1 and 2) and one immobilized species 3, where species 1 is capable of passing through 3, whereas species 2 is incapable of penetration, is almost the most general. Whatever the number of independent diffusible components the membrane divides them into these two groups. In the steady state transport case, however, conditions can vary from almost total exclusion of 2 to a case where 1 and 2 move through the matrix without change in concentration. In fact, 2 could move faster through the system than 1, but in that case the roles of 1 and 2 would merely invert.

For no concentration change, we must have $J_D = 0$ which, see eq 45, implies

$$L_p\sigma = 0 \qquad \eta L_p \to 0$$

Hence from eq 47 and 48, we must have

$$\hat{f}_{13} = \hat{f}_{23} \qquad \hat{f}_{21} \to \infty$$

It is thus in principle impossible to achieve a "no separation" case in any absolute sense. For practical purposes, however, we can expect that when a solute/solvent pair have

$$\hat{f}_{21} \gg \hat{f}_{23} = \hat{f}_{13}$$

only a minimum shift in concentration will arise.

An effectively nonseparable solute could then be "added" to the solvent and the mixture in its fixed proportion treated as the new "solvent". Such a step is thermodynamically permissible and meaningful.

If the mixture is even more complex, but all the solutes obey the no separation rule, this step is still permissible and the single "solvent" would in that case be even richer. Note, however, that it is the matrix 3 and its interaction with the mixture which decides whether in equilibrium or in flow the mixture is "one component" or more.

If impermeant species are added to the "solvent" in the phase outside the matrix, again no departure from the simple solvent/matrix case discussed in the first part will arise. Should, however, a solute be added which will only partially be separated from the "solvent" in the matrix, the three-component case discussed in the second part above will be recovered. Here too, however, a set of components 2 may be added which, with respect to their interaction with the "solvent" and the matrix, are identical. Such a situation is less likely to arise in practice than in the case of a mixed "solvent", but in principle at least the "solute" too could be complex and so indeed can the network, provided all its components are immobilized and relatively uniformly distributed.

With these generalizations, but bearing these and earlier assumptions in mind, more complex practical cases, which arise in biology or technology, can sometimes be discussed with success.[3,6,7,11]

Conclusions and Summary

We have expressed the phenomenological forces X_V and X_D in terms of the three (not two) gradients $(-\nabla p)$, $(-\nabla \Pi_2)$, and $(-\nabla \Pi_3)$, which are important. We have shown that $(-\nabla p)$ is related to the gradient in network component extra stress $(-\nabla s)$ and that the pressure level in the network, with respect to some external reference solution, with which its surface is in equilibrium, will depend upon the stress s and the need to balance chemical potentials. The network component itself will have a gradient in chemical potential $(-\nabla \mu_3/\bar{V}_3)$ per unit volume which can be finite whether the network is rigid or not. $(-\nabla \mu_3/\bar{V}_3)$ is in fact a direct measure of X_V.

The equations derived are local equations for the gradients. It is assumed that thermodynamic equilibrium exists locally, i.e., in infinitesimally thin sections normal to the gradient.

Fluxes other than J_V and J_D can easily be derived from the equations given. In particular, the flux $J_{13} = c_1\bar{V}_1 v_1$ and the flux $J_{23} = c_2\bar{V}_2 v_2$ have been given in eq 50 and 49, respectively.

The nonnegative character of the coefficients $\hat{f}_{21}$, $\hat{f}_{13}$, and $\hat{f}_{23}$[2,3] helps in the analysis. This fact also establishes the phenomenological coefficients L_p and η as nonnegative. For given gradients the sign and value of the fluxes can thus be established.

Only the highly simplified, one-dimensional stress case has been discussed.

References and Notes

(1) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.

(2) K. S. Spiegler, *Trans. Faraday Soc.*, **54**, 1409 (1958).

(3) O. Kedem and A. Katchalsky, *J. Gen. Physiol.*, **45**, 143 (1961).

(4) R. J. Bearman, *J. Phys. Chem.*, **65**, 1961-1968 (1961).

(5) N. Weiss and A. Silberberg, *Am. Chem. Soc., Symp. Ser.*,**No. 31** 69 (1976).

(6) B. W. Zweifach and A. Silberberg in "International Review of Physiology, Cardiovascular Physiology III", Vol. 18. A. C. Guyton and D. B. Young, Eds., University Park Press, Baltimore, 1979, p 215.

(7) A. G. Ogston and C. C. Michel, *Prog. Biophys. Mol. Biol.*, **34**, 197-217 (1978).

(8) D. R. Paul, *J. Polym. Sci., Polym. Phys. Ed.*, **11**, 289-296 (1973).

(9) A. Peterlin and H. Yasuda, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1215-1220 (1974).

(10) D. R. Paul, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1221-1230 (1974).

(11) A. Silberberg in "Tissue Fluid Pressure and Composition", A. R. Hargens, Ed., Waverly Press Inc., Williams and Wilkins, Baltimore, 1980, in press.

Elasticity and Stability of a Dense Gel

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ABSTRACT: An extension of the normal Gibbs formulation of statistical mechanics is applied to gels with permenent cross-links. The formalism permits an evaluation of the free energy in the case where the gel is dense, taking full account of excluded volume. This theory yields the changes in osmotic pressure upon cross-linkage and allows fully for syneresis; it enables the full elasticity of the network to be calculated, including the bulk modulus. Corrections to the simple addition of the free energy terms from network and solution theories are obtained, and for the case of a network in equilibrium with pure solvent a particularly simple formula is found.

I. Introduction

The study of the elasticity of gels comprises both the problems of rubbers and those of polymer solutions. Whereas rubbers are normally thought of as cross-linked melts whose compressibility is not interesting, once the chains are well separated by a solvent the osmotic pressure becomes a problem of great interest. Roughly speaking it is given by the difference of the positive solution pressure and the negative pressure of the network, but to explore any interactions between these two effects a joint calculation is essential. A complete stress-strain relationship for the material is then to be derived.

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*The authors consider it an honor to be invited to contribute to a celebration dedicated to Paul Flory, both on account of scientific inspiration and personal friendship.

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