

Thermodynamics of Swelling and Partition Equilibria in Gels

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The thermodynamics of swelling and partition equilibria in gels is considered. The treatment is based on the integration of the Gibbs-Duhem equation for the gel system and relates the change of the chemical potential of the gel network to the partition coefficient of the solute and to pressure changes in the gel. Thermodynamic stability conditions for swelling equilibria in gels are also considered.

Gels of crosslinked macromolecules constitute an important class of substances, which have found use in many separation processes like ion exchange, gel permeation chromatography, various membrane processes *etc.* It is therefore of importance to consider the thermodynamic aspects of the equilibrium properties of gels, in particular sorption and swelling equilibria. Although much work has been devoted to the subject in the past¹⁻⁹ many aspects have remained conceptually unclear and there is need for a rigorous thermodynamic treatment. The present work is purely thermodynamic (statistical thermodynamic aspects of the subject have recently been reviewed by Dušek and Prins¹⁰), and is based on the integration of the Gibbs-Duhem equations for a system consisting of the gel and an ambient solution.

Partition Equilibria. We consider an isothermal gel system consisting of a homogeneous gel phase (unprimed) and an ambient solution phase (primed). In the system three components are present: Gel matrix (1), solvent (2) and solute (3). The thermodynamic behaviour of the system is governed by the Gibbs-Duhem equation, applied to each homogeneous phase. For the gel phase we have

$$m_1 d\mu_1 + m_2 d\mu_2 + m_3 d\mu_3 - V dp = 0 \quad (1)$$

where m_i ($i=1, 2, 3$) is the mass of a component, μ_i its specific chemical potential, V the volume of the phase and p the pressure.

Dividing by V we obtain

$$c_1 d\mu_1 + c_2 d\mu_2 + c_3 d\mu_3 - dp = 0 \quad (2)$$

where c_i ($i=1, 2, 3$) is the concentration of a component. Concerning the choice of the composition variables it should be noted that molar concentrations/mol fractions are in general less suited for gel systems as the molecular weight of the matrix component is undefined. Also, it is more appropriate to use the weight concentration than the weight fraction, since the former is directly related to volume changes, and thus the swelling of the gel.

The concentrations in eqn. (2) are related through the equation

$$c_1 v_1 + c_2 v_2 + c_3 v_3 = 1 \quad (3)$$

where the partial specific volumes v_1 , v_2 and v_3 are assumed to be constant.

Corresponding equations are valid for the surrounding solution phase. Taking the pressure of this phase (p') as fixed, we have the equations

$$c'_2 d\mu'_2 + c'_3 d\mu'_3 = 0 \quad (4)$$

$$c'_2 v'_2 + c'_3 v'_3 = 1 \quad (5)$$

For the sake of generality, we assume here that v'_2 and v'_3 may differ from v_2 and v_3 , respectively.

The equilibrium conditions are

$$\mu_2 = \mu'_2 \quad (6)$$

$$\mu_3 = \mu'_3 \quad (7)$$

As the chemical potential of solvent in the solution phase can be determined (by vapor pressure determination, osmometry *etc.*) μ'_2 is in principle a known quantity. Thus, with the aid of eqns. (3)–(7) an integration of eqn. (2) is possible.

Choosing the solute concentration as the independent variable we obtain the following expressions for the solvent concentrations: In the solution phase

$$c'_2 = (1 - c'_3 v'_3) / v'_2 \quad (8)$$

and in the gel phase

$$c_2 = (1 - c_1 v_1 - c_3 v_3) / v_2 \quad (9)$$

Using eqns. (4)–(9) we may write

$$c_2 d\mu_2 + c_3 d\mu_3 = c_2 d\mu'_2 + c_3 d\mu'_3 = \left(\frac{1 - c_1 v_1 - c_3 v_3}{v_2} - \frac{1 - c'_3 v'_3}{v'_2} \frac{c_3}{c'_3} \right) d\mu'_2 \quad (10)$$

We now introduce the partition coefficient determining the solute distribution between the solution and gel phases:

$$c_3 = K c'_3 = \gamma (1 - c_1 v_1) c'_3 \quad (11)$$

where K is the conventional partition coefficient and γ is the "reduced" partition coefficient corrected for the volume occupied by the gel matrix. Substituting eqn. (11) into eqn. (10) we obtain

$$c_2 d\mu_2 + c_3 d\mu_3 = \left[\frac{v'_2}{v_2} - \gamma + \gamma \varepsilon c'_3 \right] \frac{1 - c_1 v_1}{v'_2} d\mu'_2 \quad (12)$$

where

$$\varepsilon = v'_3 (1 - v'_2 v_3 / v_2 v'_3) \quad (13)$$

The partition coefficient is an experimentally determinable quantity, which in general depends on the concentration c'_3 . Similarly, the volume V of the swelling gel is an experimentally determinable function of c'_3 . As

$$c_1 = m_1 / V \quad (14)$$

where m_1 is constant, also c_1 is a known function of c'_3 . We may express these functions by the series expansions

$$\gamma = \gamma_0 (1 + \alpha_1 c'_3 + \dots) \quad (15)$$

$$V = V_0 (1 + \beta_1 c'_3 + \dots) \quad (16)$$

$$c_1 = c_1^0 / (1 + \beta_1 c'_3 + \dots) \quad (17)$$

where α_1 and β_1 are experimentally determinable constants.

We also introduce an analytic expression for μ'_2 . We may use the usual representation *via* the activity coefficient or, which is more convenient, the virial expansion of the osmotic pressure:

$$\mu'_2 = (\mu'_2)' - v'_2 \pi' \quad (18)$$

where

$$\pi' = \frac{RT}{M_3} c'_3 + A_2 c'^3_3 + \dots \quad (19)$$

represents the osmotic pressure of the ambient solution, measured against pure solvent (M_3 is the molar mass of solute and A_2 the second virial coefficient).

Inserting eqn. (12), together with eqns. (15)–(19), into eqn. (2) and integrating between the limits $c'_3 = 0$ and $c'_3 = c$, we obtain

$$\int_0^c \frac{d\mu_1}{dc'_3} dc'_3 = \int_0^c \left(\frac{v'_2}{v_2} - \gamma + \gamma \varepsilon c'_3 \right) \left(\frac{1}{c_1} - v_1 \right) \times \frac{d\pi'}{dc'_3} dc'_3 + \int_{p_0}^p \frac{dp}{c_1} \quad (20)$$

where p_0 is the pressure in the gel phase for $c'_3 = 0$.

The second integral in eqn. (20) may be evaluated by term-by-term integration. Carrying out the integration to terms of second order, and evaluating the last integral by the mean value theorem for integrals, we obtain

$$\Delta\mu_1 = \left(\frac{v'_2}{v_2} - \gamma_0 \right) \frac{(1 - c_1^0 v_1) RT}{c_1^0 M_3} c + B_2 c^2 + \frac{\Delta p}{c_1^0} (1 + \beta_1 \theta c + \dots) \quad (21)$$

where

$$B_2 = \frac{RT}{2M_3} \frac{(1-c_1^0 v_1)}{c_1^0} \left[\gamma_0 (\varepsilon - \alpha_1) + \frac{2A_2 M_3 \left(\frac{v_2'}{v_2} - \gamma_0 \right) + \frac{\beta_1}{1-c_1^0 v_1} \left(\frac{v_2'}{v_2} - \gamma_0 \right)}{RT} \right] \quad (22)$$

and

$$\Delta p = p - p_0 \text{ and } 0 \leq \theta \leq 1.$$

This equation relates the partition coefficient γ_0 to changes in the chemical potential of the gel network and the hydrostatic pressure in the gel. The latter term is of particular interest, because partition of solutes induced by the "swelling pressure" of gels has been a controversial subject for a long time.¹⁻⁵ However, in freely swelling flexible gels the hydrostatic pressure in the gel phase must equal the ambient hydrostatic pressure. This may be concluded from general thermodynamic criteria for heterogeneous equilibria,¹¹ a more direct proof being given in the next section. Thus, for freely swelling gels

$$p = p_0 = p' \quad (23)$$

and the pressure term vanishes in eqn. (21). In this case the partition coefficient is directly related to the change of the chemical potential of the gel matrix.

It is of some interest to consider a completely inert gel matrix, representing an "ideal" gel system. Then

$$\Delta \mu_1 \equiv 0 \quad (24)$$

and from (21) it follows

$$\gamma_0 = \frac{v_2'}{v_2} = 1 \quad (25)$$

the last equality indicating that for a non-interacting gel matrix the partial specific volumes in the two phases have to be equal. In this case the solution inside the gel is identical with the ambient solution (from eqns. (3), (5) and (11) we obtain $c_3/c_2 = c_3'/c_2'$). More generally we have

$$\gamma_0 > \frac{v_2'}{v_2} \text{ implies } \Delta \mu_1 < 0, \quad (26)$$

$$\gamma_0 < \frac{v_2'}{v_2} \text{ implies } \Delta \mu_1 > 0 \quad (27)$$

As an example of the latter relation we may consider partition equilibria in charged gels (the present treatment is applicable to a polyelectrolyte gel-simple salt solution, where the constituents have one ion in common, since the system has three components in Gibbs sense). Because of the Donnan exclusion we always have $\gamma < 1$. Thus $\Delta \mu_1 > 0$, the chemical potential of the gel network-fixed ion system increasing on addition of a simple salt.

For dilute solutions we may write

$$\begin{aligned} \Delta \mu_1 &= \left(\frac{\partial \mu_1}{\partial c_1} \right)_0 \Delta c_1 + \left(\frac{\partial \mu_1}{\partial c_3} \right)_0 \Delta c_3 + \\ &\left(\frac{\partial \mu_1}{\partial p} \right)_0 \Delta p = - \left(\frac{\partial \mu_1}{\partial c_1} \right)_0 \frac{c_1^0}{V_0} \Delta V + \\ &\left(\frac{\partial \mu_1}{\partial c_3} \right)_0 \Delta c_3 + v_1 \Delta p \end{aligned} \quad (28)$$

where we have used eqn. (14) to obtain the last equality.

If $\gamma \equiv 0$, $\Delta c_3 \equiv 0$, and we obtain from (21), (23) and (28)

$$- \left(\frac{\partial \mu_1}{\partial c_1} \right)_0 \frac{c_1^0}{V_0} \Delta V = \frac{v_2'}{v_2} \frac{(1-c_1^0 v_1)}{c_1^0} \frac{RT}{M_3} c + B_2 c^2 \quad (29)$$

This is the basic equation for gel-osmometry.¹²⁻¹⁵ It shows that for impermeable gels the volume change of the gel is a direct measure of the osmotic pressure of the ambient solution. However, the method is not absolute, as the value of $\left(\frac{\partial \mu_1}{\partial c_1} \right)_0$ is unknown and has to be determined by calibration. Also, the second order coefficient B_2 differs from the second osmotic virial coefficient. With permeable gels interference from the solute term in eqn. (28) cannot in general be neglected and the volume change is no longer a measure of the osmotic pressure.

If in partition experiments the volume of the gel is kept constant ($c_1 \equiv c_1^0$) pressure changes in the gel phase have to be considered. In this case the full eqn. (21) applies, with $\beta_1 = 0$. In particular, for an impermeable gel $\gamma \equiv 0$, and $\Delta \mu_1 = v_1 \Delta p$

in eqn. (28). The exact integration of eqn. (20) then yields

$$\Delta p = -(\nu'_2/\nu_2)\pi' \quad (30)$$

Swelling equilibria in pure solvent. We will in this section consider swelling equilibria and pressure-volume relations for a gel immersed in a pure solvent. To derive the thermodynamic stability conditions for a gel, which has reached its equilibrium volume of swelling, we imagine that the gel is perturbed by changing its volume by a small amount δV . The work done on the gel, δw , equals the change of Gibbs free energy for the gel-solvent system:

$$\delta w = \delta G = - \int_0^{\delta V} (p-p') dV = -(\bar{p}-p')\delta V \quad (31)$$

where, by the mean value theorem

$$\bar{p} = p_0 + \theta \frac{dp}{dV} \delta V, \quad 0 \leq \theta \leq 1 \quad (32)$$

From eqn. (2) we obtain (since the solvent is still in equilibrium with the strained gel, $d\mu_2=0$)

$$dp = c_1 d\mu_1 = c_1 \left[\left(\frac{\partial \mu_1}{\partial c_1} \right)_p dc_1 + \nu_1 dp \right] \quad (33)$$

Or, with the aid of eqn. (14)

$$\frac{dp}{dV} = - \frac{c_1^2}{(1-c_1\nu_1)V} \left(\frac{\partial \mu_1}{\partial c_1} \right)_p \quad (34)$$

Thus

$$\delta G = -(p_0-p')\delta V + \frac{\theta c_1^2}{(1-c_1\nu_1)V} \left(\frac{\partial \mu_1}{\partial c_1} \right)_p (\delta V)^2 \quad (35)$$

At equilibrium G has a minimum, which implies

$$\delta G > 0 \quad (36)$$

for all variations δV . This is true only if

$$p_0 = p'; \quad \left(\frac{\partial \mu_1}{\partial c_1} \right)_p > 0 \quad (37)$$

Thus, in a flexible gel at equilibrium the hydrostatic pressure is necessarily equal to the surrounding pressure. Furthermore, from eqns.

(34) and (37) it follows that the pressure increases on compression and decreases on dilation. The straining of a gel thus induces pressure changes which may be designated the "swelling pressure" of a gel. In unstrained gels the term has no physical significance.

It should be noted that the above relations are valid for a gel where the components are truly integrated into a single homogeneous phase. This is a prerequisite for the Gibbs-Duhem equation to be valid. If all the straining forces are balanced by stresses set up in the gel matrix (like in a system of springs) the latter has to be considered as a separate phase. In this case the change in its chemical potential is not coupled to pressure changes, the hydrostatic pressure in the pore liquid in general being equal to the external pressure. Such a gel is, of course, heterogeneous.

Finally, it should be noted that from the thermodynamic point of view, a gel should always be considered in conjunction with its solution phase. This is an immediate consequence of the Gibbs phase rule:

$$f = r + 2 - g \quad (38)$$

where f is the number of degrees of freedom, r the number of components and g the number of phases. For a polymer solution, prior to cross-linking, $r=2$ and $g=1$. Thus $f=3$, representing an independent choice of temperature, pressure and concentration. After crosslinking one degree of freedom is lost, as the concentration of the gel can no longer be independently changed. Thus $f=2$ and $g=2$ in eqn. (38). This means that a gel should always be considered as being in contact with a solution phase (syneresis seems to be a manifestation of this tendency). Vapor phase equilibria with *homogeneous* gels therefore seem to be inadmissible thermodynamically, leading inevitably to the formation of heterogeneities in the gel.

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Received June 14, 1982.