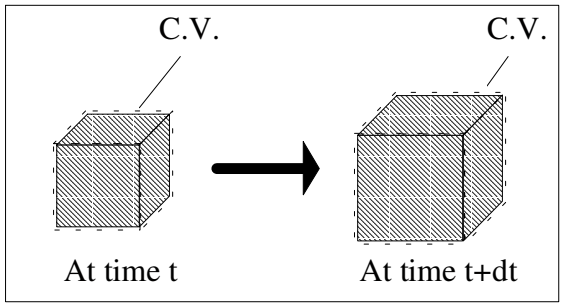
Bond Graph Modeling of Electrolyte Gel



System: (Polymer gel network + solvent inside) inside the control volume (c.v.)., i.e., the control volume is changing as the get network is expanding due to absorbing the surrounding solvent fluid.

Additional Modeling Assumptions:

- The characteristic length of gel element is much greater that the Debye length.
- The gel element's ionic concentration boundary condition is described by Donnan equilibrium law.
- The ionic concentrations inside the gel is uniform at any instant of time.

Gel/Membrane Interface

Donnan Equilibrium Theory and Electroneutrality

The Donnan membrane equilibrium phenomena is due to the balance between the diffusion tendencies and the electrical attraction/repulsion among ions/fixed charge groups. Since the equilibrium condition require the ions in both regions to have equal potential while also requiring to satisfy the electroneutrality condition, the electric potential develop across the gel/membrane interface. It should be noted that the macroscopic electroneutrality is valid for dimensions much greater than the Debye length.

Consider the ionic gel immersed in ionic solvent bath as shown above. Assuming the concentration of the mobile ions in both the gel and the solvent bath are much smaller that the concentration of polymer or solvent, the mobile ion concentration can be considered as dilute, and the electrochemical potential of the ions can be described by

$$\mu_i = \mu_i^o + RT\ln(a_i) + z_i F\phi_i$$

where μ_i is the electrochemical potential of the ion,

μ_i^o is the chemical potential of the pure ion species,

R is the universal gas constant,
T is the temperature,
a_i is the activity coefficient of the ion,
z_i is the ionic valence,
F is the Faraday constant, and
φ_i is the electrical potential of the ion.

When the electrolyte in both the gel and the bath is in true equilibrium, the electrochemical potential of the ion in the bath will be equal to the electrochemical potential of the ion inside the gel.

$$\mu_i^g = \mu_i^b$$

where μ_i^g is the electrochemical potential of the ion inside the gel, and
μ_i^b is the electrochemical potential of the ion in the solvent bath.

or, since μ_i^o is the same for the *g* and *b* phases, we have

$$RT\ln(a_i^g) + z_i F\phi_i^g = RT\ln(a_i^b) + z_i F\phi_i^b$$

or

$$\frac{RT}{z_i F}\ln(\frac{a_i^g}{a_i^b}) = \Delta\phi_i$$

where $\Delta\varphi_i$ is $\varphi_i^b - \varphi_i^g$, the electrical potential difference across the gel-bath interface. Since this electrical potential difference is common to all ions, the activity coefficient ratio across the interface of different ions, say *i* and *j*, can be related as

$$\frac{1}{z_i}\ln(\frac{a_i^g}{a_i^b}) = \frac{1}{z_j}\ln(\frac{a_j^g}{a_j^b})$$

For the 1:1 electrolyte where $z_i = 1$ and $z_j = -1$, the above expression reduces to

$$a_i^g a_j^g = a_i^b a_j^b$$

For the case where the activity coefficients in the *g*- and *b*-phases are equal or for the ideal dilute solution case, we can also write

$$x_i^g x_j^g = x_i^b x_j^b$$

or

$$c_i^g c_j^g = c_i^b c_j^b$$

where x_i^g, x_i^b, c_i^g, c_i^b are the mole fractions and concentraions of the ion *i* in the gel and the bath, and
x_j^g, x_j^b, c_j^g, c_j^b are the mole fractions and concentraions of the ion *j* in the gel and the bath, respectively.

The electroneutrality conditions of both the bath and the gel are

$$\Sigma z_i F c_i = 0 \text{ for external bath}$$
$$\Sigma z_i F \bar{c}_i + \bar{\rho}_m = 0 \text{ for inside the gel/membrane}$$

where $\bar{\rho}_m$ is the fixed charge group density, and $\bar{c}_i$ is the ion concentration inside the gel/membrane.

The Donnan equilibrium and electroneutrality conditions, along with charge conservation relations, can be used to compute individual ion concentrations. Stictly speaking, the above result applies to true equilibrium case. However, in general, it can also be applied to non-equilibrium case as long as the net transport is much slower than the diffusion or the drift components of the transport process.

Ion Transport

The transport of ions due to diffusion and migration in the electrolytic medium is described by widely used relation (neglecting the connective contribution)

$$\Gamma_i = -D_i \nabla c_i - \frac{z_i}{|z_i|} u_i c_i \nabla \phi$$

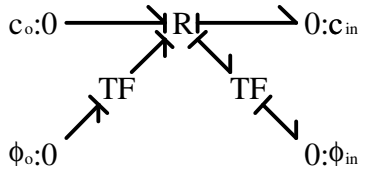
where Γ_i is the molar flux of the ith species ion,
D_i is the diffusion coefficient,
c_i is the concentration,
u_i is the mobility,
z_i is the valence of the ith species,
φ is the electrical potential.

Assuming both the concentration and electrical potential gradient inside the gel near its interface is linear and considering only one dimensional case for simplification, then the average ion transport into the gel at the interface can be written as

$$\bar{\Gamma}_i = -\bar{D}_i \frac{\Delta \bar{c}_i}{\Delta x} - \frac{z_i}{|z_i|} \bar{u}_i \bar{c}_{i,avg} \frac{\Delta \phi}{\Delta x}$$

where $\Delta \bar{c}_i, \Delta \phi$ is the ion concentration and electrical potential differences between inside the gel near its interface and outside bath, i.e. $\bar{c}_{i,inside} - c_{i,bath}, \phi_{inside} - \phi_{bath}$, and Δx is the distance in between. The first term describes the diffusion component due to the

concentration gradient, and the second term describes the migration component due to the electric potential gradient. Since the electric potential gradient is commonly experienced by all ions, it is the source of coupling effect among ions. Studying the expression for the ion transport above, one can easily represent this using the bond graph structure



Electroneutrality: Electric Potential Coupling

The ions with greater diffusivity will tend to move across the medium at faster rate than the ions with lower diffusivity. However, such tendency for charge separation induces local electric field among ions, and it in turn acts to retard the faster ions and to accelerate the slower ions. For instance, if the faster ions are positively charged whereas the slower ions are negatively charged, then positive local electric potential gradient will build up to retard the positive ions and to accelerate the negative ions. Such "local" electric field, which acts in the scale of a few Debye length, is quite large and it is rather difficult to induce charge separation in macroscopic scale. Therefore, in macroscopic scale, the electroneutrality prevails.

The electrical potential coupling among ions can be modeled as a simple ideal parallel plate capacitor (Oster)

$$\Delta\phi_e = \frac{1}{C_E}\sum_i q_i$$

$$C_E = \frac{\varepsilon A}{d}$$

where $\Delta\varphi_e$ is the induced electric potential,

C_E is the electric potential coupling capacitance,

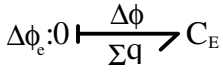
ε is the dielectric constant of the electrolyte,

A is the cross-sectional area of the ion transport,

d is the typical maximum separation of charges in a volume element, ~ 10^{-8},

q_i is the charge of the ion.

The bond graph representation is simply



Note that the induced electric potential $\Delta\varphi_e$ here only models the aporoximate effect of bulk electroneutrality in uniform medium, and therefore it does not model the electric potential difference between two regions of different medium.

Macroscopic Electric Potential Gradient

In addition to the macroscopic electroneutrality coupling among ions in each region of uniform electrolytic medium (bulk electroneutrality), there also exists electric potential gradient between two regions of unequal ion concentrations. For example, the Donnan equilibrium membrane potential is the electric potential difference across the membrane induced by the balance between the individual ion diffusion tendencies and the bulk electroneutrality in each region. In order to describe the electric potential profile exactly, one needs to solve the Gauss' law which relates the electric field gradient to the net charge at a point

$$\nabla \bullet \varepsilon E = -\frac{1}{\varepsilon}\nabla^2\phi = \rho_u$$

where ρ_u is the net charge (in fact, the electroneutrality effect in previous section may also be solved using Gauss' law directly). However, not only the analysis is non-trivial and computation intensive, the exact electric potential profile is not of concern for our purpose. Therefore, we will model the electric potential difference between two uniform media region as the average of the individual ion specie's contribution at near equilibrium (quasistatic) condition, i.e., the individual ion contribution and the average electric potential difference are modelled as

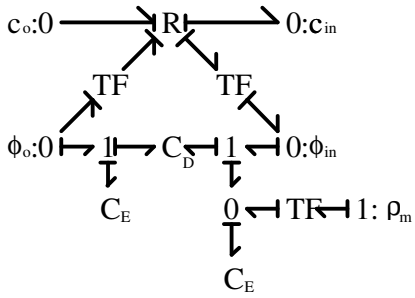
$$\Delta\phi_i \cong \frac{RT}{z_i F}\ln\left(\frac{x_{io}}{\bar{x}_i}\right)$$

$$\Delta\phi_{avg} \cong \frac{1}{n}\sum_i^n \frac{RT}{z_i F}\ln\left(\frac{x_{io}}{\bar{x}_i}\right)$$

At any instant, the total electric potential difference is then the sum of $\Delta\varphi_{avg}$ and $\Delta\varphi_e$.

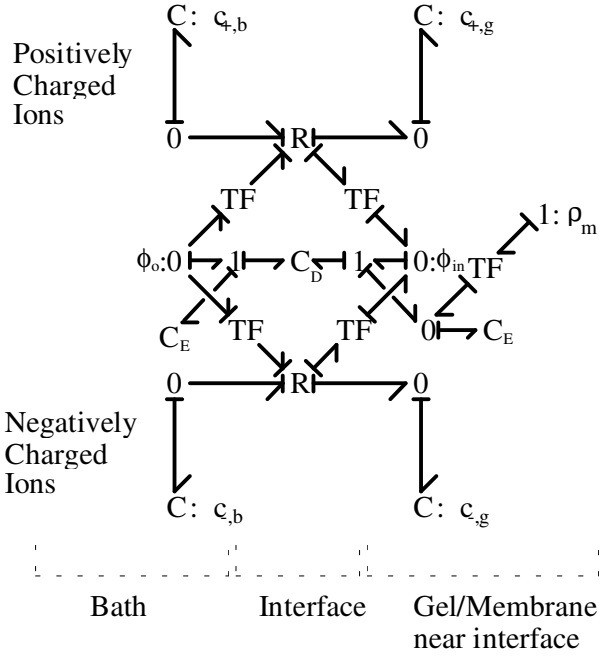
$$\Delta\phi \cong \frac{1}{n}\sum_i^n \frac{RT}{z_i F}\ln\left(\frac{x_{io}}{\bar{x}_i}\right) + \frac{1}{C_E}\left(\sum_i q_i + q_m\right)$$

The bond graph representation of the total electric potential across interface is then

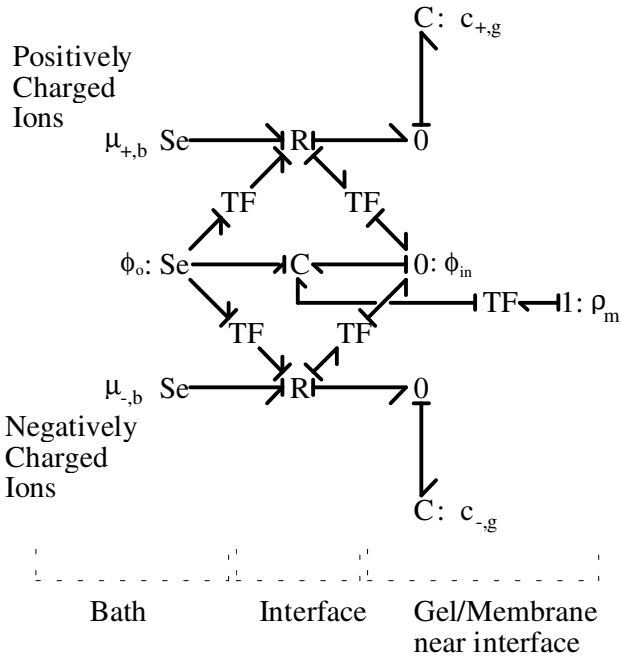


Dynamic Model: Bond Graph Representation

Applying the above bond graph structures to the case of 1:1 electrolyte transport at the gel/membrane interface, we then have



In most cases, the external solvent bath may be modelled as the ideal ions/solvent source as well as the electric potential reference ground, in which case the bond graph representation then simpliflies to



Dynamic Model: System Equations

Chemical Capacitances:

With the assumption of dilute solution, the chemical potential of ion in the gel may be described by

$$\mu_{c,i} = \mu_i^o + RT \ln x_i$$

Treating the polymer molecule as solvent/ion size molecule with equivalent scaling factor, x, the effective mole fraction of ion, x_i is then

$$x_i \cong \frac{n_i}{n_s + xn_p + \sum n_j} \cong \frac{n_i}{n_s + xn_p}$$

and

$$\mu_{c,i} = \mu_i^o + RT \ln\left(\frac{n_i}{n_s + xn_p}\right)$$

Safely assuming the solvent concentration changes at much slower rate than the individual ion concentration, the rate of change of ion's chemical potential may be approximated by

$$\frac{d\mu_{c,i}}{dt} \cong RT \frac{d}{dt}\left[\ln\left(\frac{n_i}{n_s + xn_p}\right)\right] \approx \frac{RT}{n_i}\frac{dn_i}{dt}$$

Electrical Capacitances:

As mentioned previously, the capacitance field describing the Donnan potential and the electroneutrality is expressed as

$$\Delta\phi \cong \Delta\phi_D + \Delta\phi_E \cong \frac{1}{n}\sum_i^n \frac{RT}{z_i F}\ln\left(\frac{x_{io}}{\bar{x}_i}\right) + \frac{1}{C_E}\left(\sum_i q_i + q_m\right)$$

or

$$\Delta\phi \cong \Delta\phi_D + \Delta\phi_E \cong \frac{1}{n}\sum_i^n \frac{RT}{z_i F}\left[\ln\left(x_{io}\right) - \ln\left(\frac{n_i}{n_s + x n_p}\right)\right] + \frac{1}{C_E}\left(\sum_i z_i n_i + z_m n_m\right)$$

The rate of change of electric potential difference is then

$$\frac{d(\Delta\phi)}{dt} \cong -\frac{1}{n}\sum_i^n \frac{RT}{z_i F n_i}\frac{dn_i}{dt} + \frac{1}{C_E}\left(\sum_i z_i \dot{n}_i + z_m \dot{n}_m\right)$$

Resistance:

The ion transport kinetics of the resistive element is simply

$$\frac{dn_i}{dt} = K_i\left[\left(\mu_{c,io} - \mu_{c,i}\right) - z_i F\Delta\phi\right]$$

The resulting system equations for the case of 1:1 binary electrolyte are

$$\frac{d\mu_{+,g}}{dt} \approx \frac{RT}{n_{+,g}}\frac{dn_{+,g}}{dt}$$

$$\frac{d\mu_{-,g}}{dt} \approx \frac{RT}{n_{-,g}}\frac{dn_{-,g}}{dt}$$

$$\frac{d(\Delta\phi)}{dt} \cong -\frac{1}{2}\frac{RT}{F}\left[\frac{1}{n_{+,g}}\frac{dn_{+,g}}{dt} - \frac{1}{n_{-,g}}\frac{dn_{-,g}}{dt}\right] + \frac{1}{C_E}\left(\frac{dn_{+,g}}{dt} - \frac{dn_{-,g}}{dt} + z_m\frac{dn_m}{dt}\right)$$

where

$$\frac{dn_{+,g}}{dt} = K_+\left[\left(\mu_{+,b} - \mu_{+,g}\right) - F\Delta\phi\right]$$

$$\frac{dn_{-,g}}{dt} = K_-\left[\left(\mu_{-,b} - \mu_{-,g}\right) + F\Delta\phi\right]$$

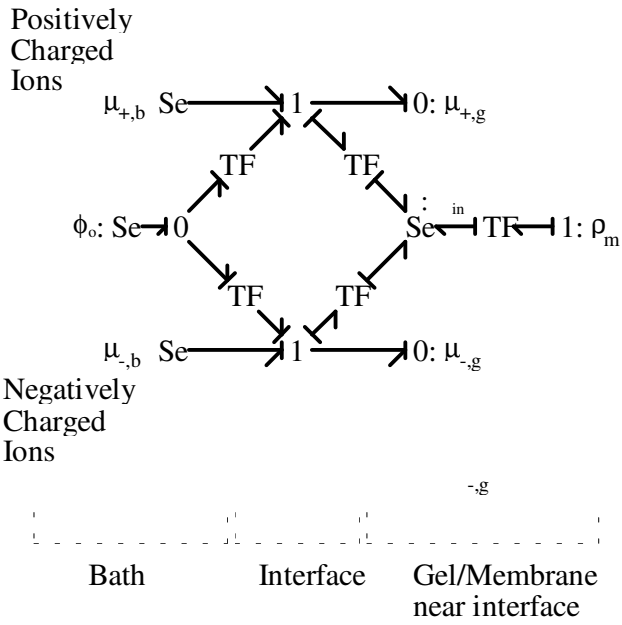
$$n_{+,g} = \exp\left[\frac{\left(\mu_{+,g} - \mu_+^o\right)}{RT} + \ln\left(n_s + x n_p\right)\right]$$

$$n_{-,g} = \exp\left[\frac{\left(\mu_{-,g} - \mu_{-}^{o}\right)}{RT} + \ln\left(n_s + x n_p\right)\right]$$

For the quasi-equilibrium case where the fixed charge density does not vary with time, the above result then reduces to the Donnan equilibrium condition and the electroneutrality.

$$x_{+g} x_{-g} = x_{+b} x_{-b}$$
$$n_{+g} - n_{-g} + z_m n_m = 0$$

It should be noted that the transport rate of establishing Donnan equilibrium condition is extremely fast due to large local electric field coupling among ions/fixed charged groups within the Debye length of the solvent bath/gel interface. Therefore, in most case, the Donnan equilibrium condition and the bulk electroneutrality is valid even in the non-equilibrium case with net transport, and they may be employed as the boundary conditions for the state of gel/membrane's bulk. In such cases, the combined effect of Donnan equilibrium condition and bulk electroneutrality can be treated as effort (electric potential) source, and the bond graph representation further reduces to



The electric potential source term on the right hand side exerts the necessary electric potential on the ions based on the concentrations of the both positive and negative ions and membrane fixed charges to achieve both the Donnan equilibrium condition and bulk electroneutrality, i.e., combining the bulk electroneutrality and Donnan equilibrium condition yields the mole fractions and the electric potential of the ions

$$x_{+g} - x_{-g} + x_m = 0$$

$$x_{+o}x_{-o} = x_{+g}x_{-g}$$

$$x_{+g} = \frac{\sqrt{x_m^2 + 4(x_{+o}x_{-o})} - x_m}{2}$$

$$x_{-g} = \frac{\sqrt{x_m^2 + 4(x_{+o}x_{-o})} + x_m}{2}$$

$$\Delta\phi = \frac{RT}{F}\ln\left(\frac{x_{+o}}{x_{+g}}\right) = \frac{RT}{F}\ln\left(\frac{x_{-g}}{x_{-o}}\right)$$

One should note that the energy dissipation and entropy generation due to the diffusion process is assumed to be unimportant and thus left out from this quasi-equilibrium model.

Gel/Membrane Bulk

Electroneutrality and Ion Transport

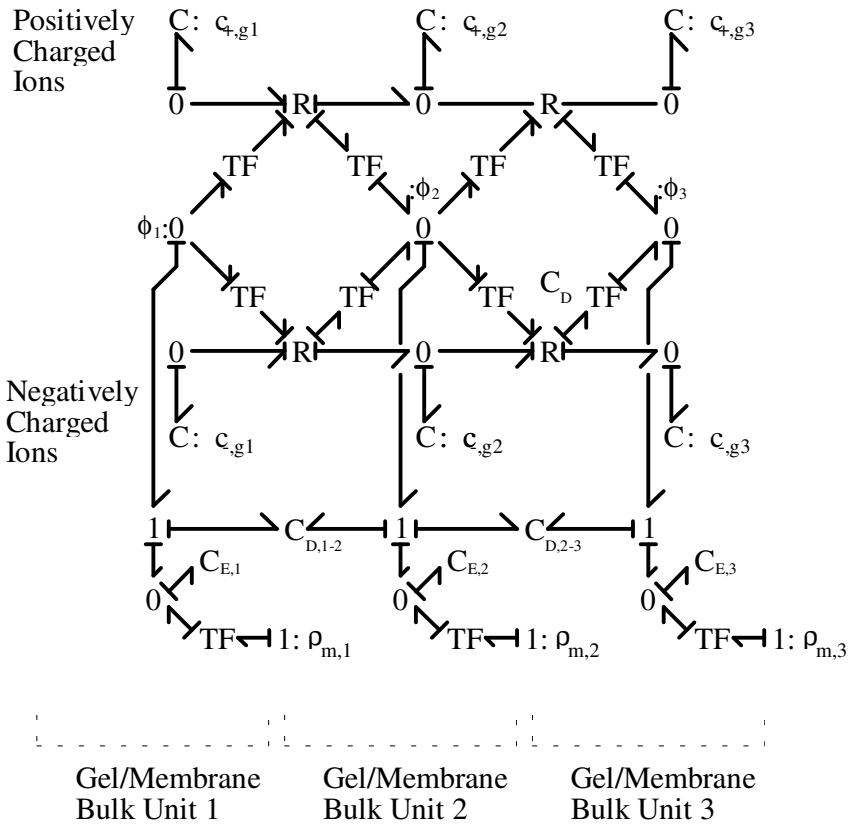
The bulk of the gel/membrane model is identical to the gel/membrane interface model discussed in previous section. It is assumed to be quasistatic with uniform state properties such as ion/solvent concentrations, fixed charge density, and temperature, and as with the interface, the strong electric field coupling among ions and fixed charged prevails inducing macroscopic bulk electroneutrality at equilibrium

$$\Sigma z_i F\overline{c}_i + \overline{\rho}_m = 0$$

and ion transport is described by

$$\overline{\Gamma}_i = -\overline{D}_i\frac{\Delta\overline{c}_i}{\Delta x} - \frac{z_i}{|z_i|}\overline{u}_i\overline{c}_{i,avg}\frac{\Delta\phi}{\Delta x}$$

The bond graph structure of three gel/membrane bulk units connected in series is



According to above bond graph model, note the electric potential differences can exist among the bulk units during the transport process since the internal pH and subsequently the fixed charge density of each unit may well differ among units. This electric potential differences would vanish at equilibrium, though. The governing equations of each bulk unit are identical to the ones for the interface unit.

Ion Diffusion/Reaction

As the ion moves into the gel/membrane network, it may also react with the fixed charged side groups. Namely diffusing H^+ or OH^- in solvent can react with corresponding conjugate basic or acidic structures on the network, and it was shown that such diffusion-reaction can significantly slow down the overall ion transport process (Grodzinsky). As the ions are moving into the gel/membrane network while reacting with the fixed charges of network simultaneously, not only the overall kinetic of the ion's transport is affected, also the concentrations of both the mobile ions and the fixed charge groups are changed as well, subsequently changing the overall equilibrium behavior. Therefore, proper integration of the dynamic model of ion diffusion/reaction process is necessary.

Chemical Reaction

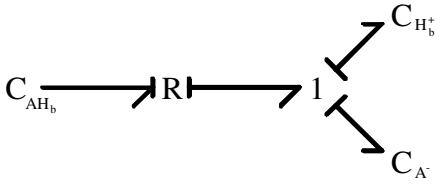
Assuming the predominant chemical reaction is the acid/base reaction between the H^+/OH^- and the fixed charge groups, we will limit the discussion to acid/base reaction only. However, the results can easily be translated to other types of reactions as well.

In acidic (or basic) environment, there are two reactions occuring simultaneously. First, the neutral side group of gel/membrane network can dissociate into the anion and the hydronium ion

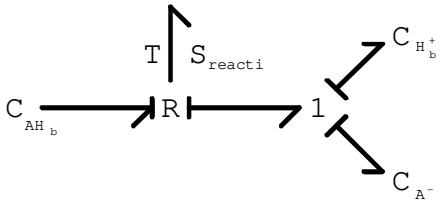
$$AH_b \Leftrightarrow A^- + H_b{}^+$$

where AH_b is the neutral side group of gel network,
A^- is the network-bound anion,
H_b^+ is the hydronium ion originally bound to Ah_b.

The bond graph representation of the reaction (Wyatt) is



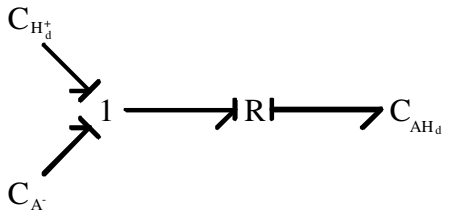
The chemical reaction is represented by a two-port resistance field, and the thermal (entropy generation) port is not included. In the case where the thermal port is of importance, it can be modified as



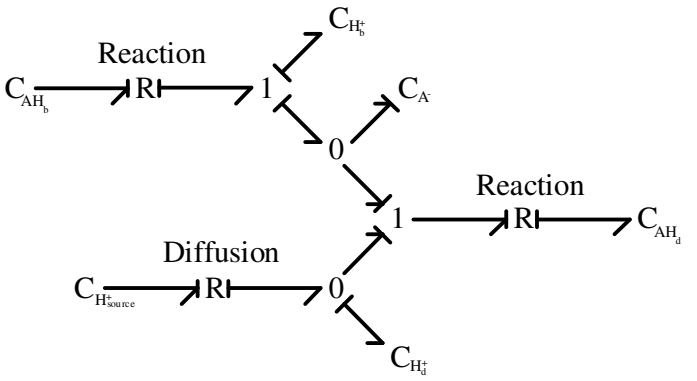
Second, the hydronium ion diffusing in from outside can associate with the network-bound anion, A^- to form the neutral side group.

$$A^- + H_d{}^+ \Leftrightarrow AH_d$$

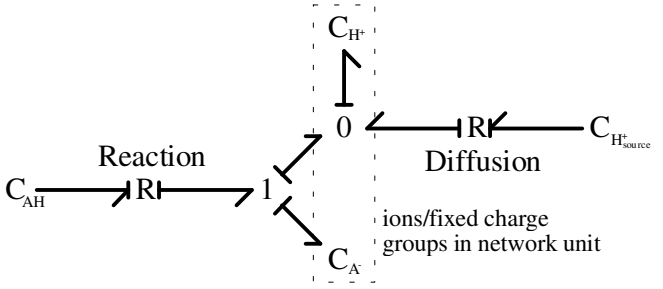
where H_d^+ is the hydronium ion diffusing into the gel network,
AH_d is the neutral side group formed.
and, the corresponding bond graph representation is



Combining the above two reactions, we have



Since H_d^+ is identical to H_b^+, the overall bond graph representation of diffusion/reaction simplies to



Chemical Reaction Kinetics

According to the simple mass-action law for elementary chemical reaction such as

$$AH \underset{k_r}{\overset{k_f}{\Leftrightarrow}} A^- + H^+$$

where k_f is the forward reaction constant, and
k_r is the reverse reaction constant,

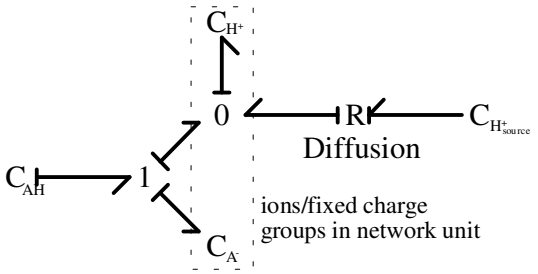
the reaction kinetic is expressed as

$$\frac{\partial [AH]}{\partial t} = k_r [A^-][H^+] - k_f [AH]$$

The equilibrium constant K_{eq} in this case would then be

$$K_{eq} = \frac{k_f}{k_r} = \frac{[A^-][H^+]}{[AH]}$$

Note in many cases, simplifications can be made with assumption that the reaction occurs at much faster rate than the diffusion, and thus can be considered as "instantaneous" and "always" at equilibrium (quasi-equilibrium). This does not imply that the concentrations of $-A^-$, H^+ or -AH do not vary with time, but they change at a rate much slower than the reaction rate, limited by the diffusion of the hydronium ion into the gel/membrane unit. For such quasi-equilibrium reaction, the bond graph representation of the diffusion-reaction then reduces to



As with the Donnan quasi-equilibrium model considered previously, the dissipated energy (heat of reaction) and the entropy generation is assumed to be unimportant in the overall dynamics of the ion's transport for the quasi-equlibrium chemical reaction model. This quasi-equilibrium reaction model shown above says at every instant of time

$$\mu_{AH} = \mu_{H+} + \mu_{A-}$$

or

$$\mu^o_{AH} + RT\ln[AH] = \mu^o_{H+} + RT\ln[H^+] + \mu^o_{A-} + RT\ln[A^-]$$

$$\frac{[H^+][A^-]}{[AH]} = \exp\left(\frac{\mu^o_{AH} - \mu^o_{H+} - \mu^o_{A-}}{RT}\right) = K_{eq}$$

Since the total possible number of the binding site -A is fixed

$$[A_{Total}] = [A^-] + [AH]$$

the equilibrium constant K_{eq} can also be written as

$$\frac{[H^+][A^-]}{[A_{Total}]-[A^-]} = K_{eq}$$

or

$$[A^-] = \frac{[A_{Total}]K_{eq}}{[H^+]+K_{eq}}$$

Differentiating this with respect to time, we get

$$\frac{d[A^-]}{dt} = -\frac{d[AH]}{dt} = -\frac{[A_{Total}]K_{eq}}{\left([H^+]+K_{eq}\right)^2}\frac{d[H^+]}{dt}$$

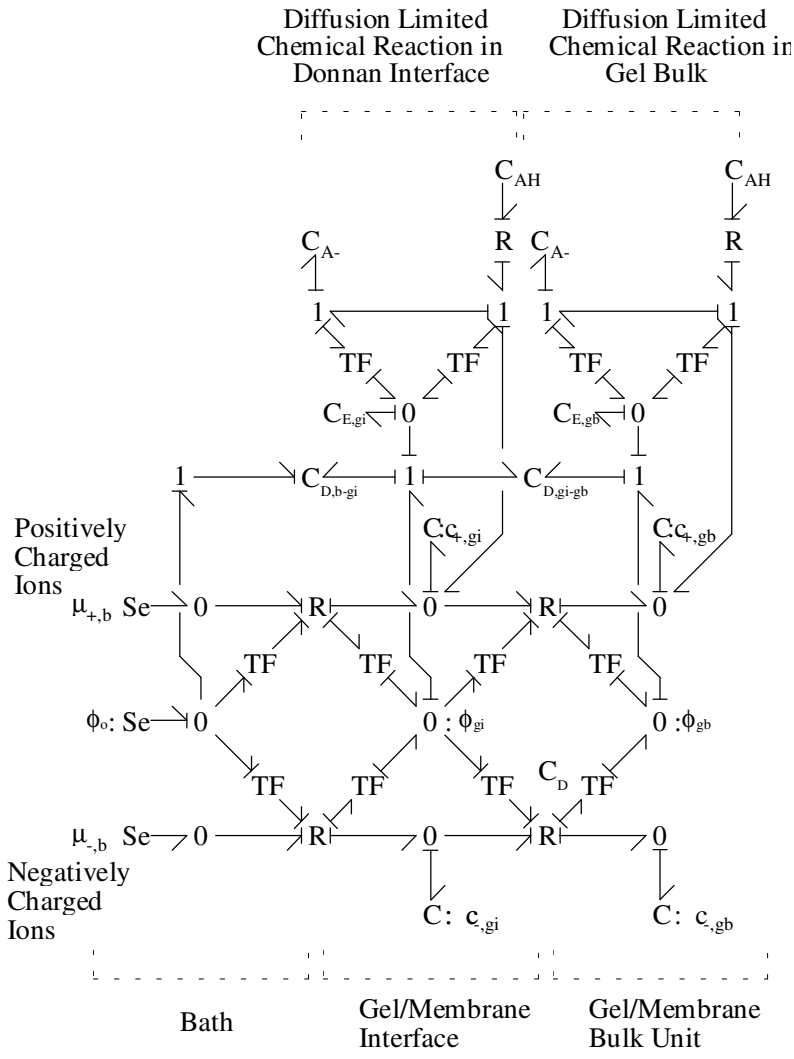
or

$$\frac{d[AH]}{dt} = \frac{[A_{Total}]K_{eq}}{\left([H^+]+K_{eq}\right)^2}\frac{d[H^+]}{dt}$$

Note that the above result is in agreement with the bond graph model which shows that only two out of total three capacitances have integral causality implying only two capacitances are independent energy storage elements whereas the other one is dependent.

Bond Graph Representation: Gel Interface, Bulk, and Chemical Reaction

Combining the models of the gel/membrane's Donnan interface and the bulk with the diffusion limited chemical reaction described above for the case of binary solution (H^+, Cl^-), we arrive at the following model. The chloride ion is a completely dissociated ion of the strong acid, HCl, and is assumed not to react or bind with other ions or fixed charges. The dissociation of gel bound groups -AH produces fixed charges $-A^-$ and hydronium ion H^+ which in turn influences the ion transport in the gel through changing both the H^+ concentration and the electric potential. The electric field coupling, however, does not affect the dissociation chemistry of -AH since the valences of produced charges are exactly opposite (i.e. +1 for H^+ and -1 for $-A^-$) and therefore their electrical effects cancel each other out exactly. For the complete model of polyelectrolyte gel, following model needs to be incorporated into the model describing the swelling behavior of the gel.



Thermodynamics of Electrolyte Gel Swelling and Ionic Contribution

Mixing/Diffusion Process

Similarly to the nonelectrolyte gel model, the quasistatic differential energy change of the control volume due to the mixing/diffusion within the gel itself can be expressed as

$$\frac{dU_M}{dt} = T\frac{dS_M}{dt} + \mu_s \frac{dn_s}{dt} + \mu_i \frac{dn_i}{dt}$$

Since the ion concentration inside the gel is much less than the concentrations of either the polymer or the solvent, the contribution of ions to the change in free energy is assumed to be additive (Flory), i.e.,

$$G_{initial} = G_s^o + G_p^o + G_i^o$$

$$G_{final} = G_s + G_p + G_i$$

$$\Delta G_M = G_{final} - G_{initial} = \left[\left(G_s + G_p\right) - \left(G_s^o + G_p^o\right)\right] + \left(G_i - G_i^o\right)$$

Note the first term in the bracket of right hand side is the ΔG_M for the nonelectrolyte gel.

$$\Delta G_M = \Delta G_{M,nonel} + n_i \Delta \mu_i$$

Similary, the entropy change due to mixing is

$$\Delta S_M = \Delta S_{M,nonel} + n_i \Delta s_i$$

or

$$\Delta S_M = \Delta S_{M,nonel} + n_i \frac{\Delta \mu_i}{T}$$

where the ionic contribution to enthalpy change is assumed to be zero and the second term on right hand side represents the entropy generated due to mixing of ion within the gel. In addition, the ionic contribution to the chemical potential change of the solvent is also assumed to be additive (due to sufficient dilution of ions)

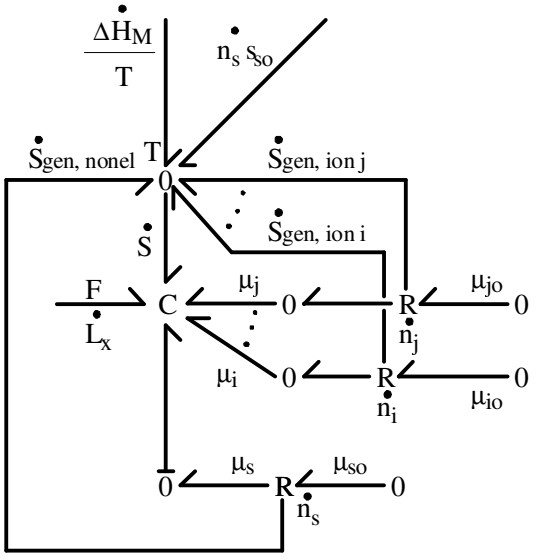
$$\mu_s - \mu_s^o = \left(\Delta \mu_s\right)_{nonel} + \left(\Delta \mu_s\right)_{ion}$$

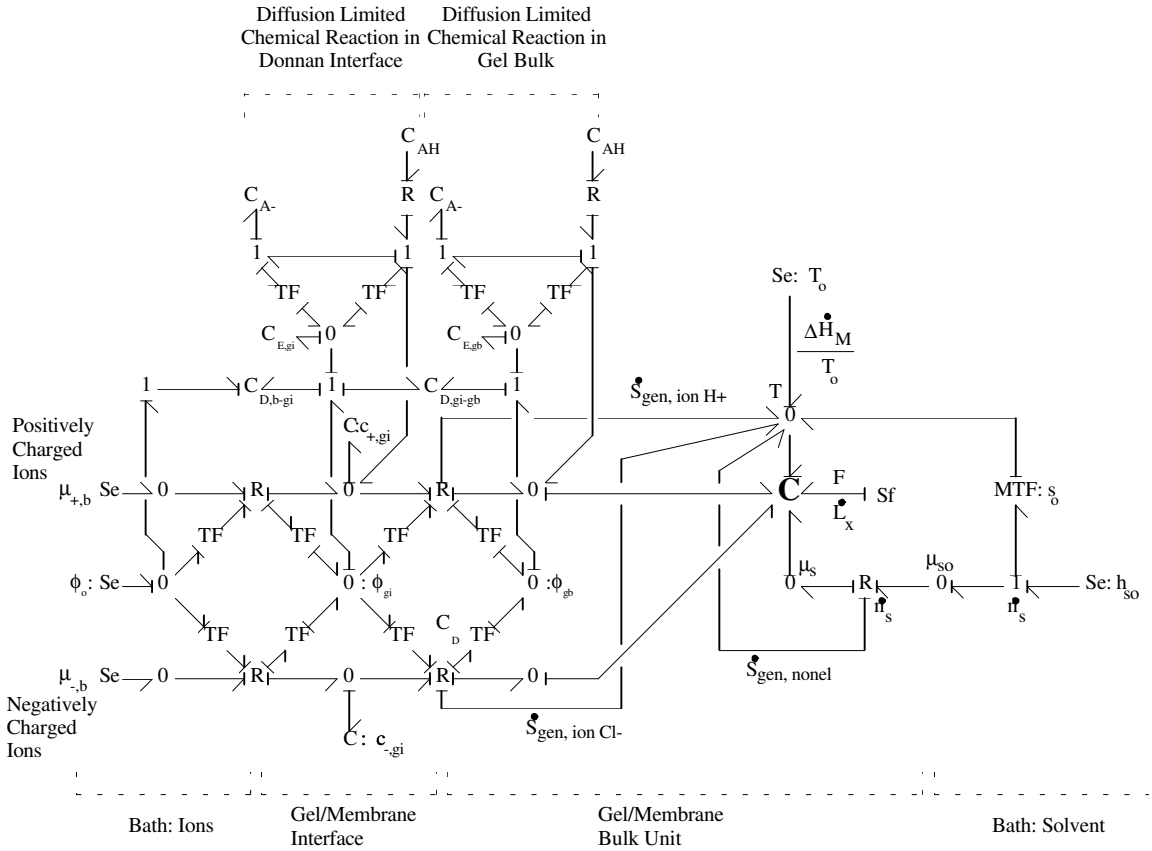
where

$$\left(\Delta \mu_s\right)_{ion} \cong -v_1 RT \sum c_{ion} \quad \text{(van't Hoff equation)}$$

Bond Graph Representation

The bond graph representation of the polyelectrolyte gel's mixing process derived above can be expressed as



Overall Process: Bond Graph Representation

Combining the above results for the binary mobile ion specie case, we have