

THE DONNAN EQUILIBRIUM

J. Th. G. Overbeek

CONTENTS

	<i>Page</i>
I. INTRODUCTION	58
II. ELEMENTARY THEORY	58
III. EQUILIBRIUM AND NON-EQUILIBRIUM PROPERTIES	61
IV. INTRODUCTION OF ACTIVITY COEFFICIENTS	63
V. APPROACH BASED UPON DETAILED CONSIDERATION OF THE UNEQUAL DISTRIBUTION OF IONS IN THE IONIC ATMOSPHERES	64
5.1 Theory	64
5.2 Qualitative treatment for the distribution of ions	64
5.3 Qualitative treatment of osmotic pressure	66
5.4 Quantitative treatment of the distribution of ions	67
5.5 Higher concentrations of the non-diffusible ions	69
5.6 Strong interaction of double layers	71
5.7 Activity coefficients	71
5.8 Experimental data	71
VI. THE DONNAN POTENTIAL	74
6.1 On the location of the Donnan potential	74
6.2 Formulation of the Donnan e.m.f.	75
6.2.1 Ideal solutions	77
6.2.2 Deviations from ideal behaviour	78
6.3 Experimental evidence	79
6.4 On the limited use of determining Donnan e.m.f., suspension effect or pH of a suspension	81
VII. SOME REMARKS ON BIOLOGICAL APPLICATIONS	82
REFERENCES	82

THE DONNAN EQUILIBRIUM

J. Th. G. Overbeek

1. INTRODUCTION

When two coexistent phases are subject to the restriction that one or several of the ionic components cannot pass from one phase into the other, a particular equilibrium is set up, called Donnan equilibrium. As a rule the restriction is caused by a membrane, permeable to the solvent and to small ions, but impermeable to ions of colloidal size, and therefore these equilibria are often called Donnan *membrane equilibria*. The presence of a membrane is, however, not essential. In a gel or a resin in which the structural component is charged, and even in a sediment of a substance like clay dissociating into very large and small ions the equilibria are of the Donnan type.

The Donnan equilibrium has three important aspects, viz.

1. The unequal distribution of ions.
2. The osmotic pressure.
3. The potential difference between the phases.

The elementary theory of the Donnan equilibrium⁽¹⁾ for ideal solutes is known well enough. As, however, electrolytes of colloidal size are usually far from ideal, it is important to investigate how this lack of ideality affects measurable properties. In the present article we shall therefore lay particular stress on the quantitative treatment of non-ideal systems.

2. ELEMENTARY THEORY

The conditions for the Donnan equilibrium are conveniently described by means of the electrochemical potentials η_j introduced by GUGGENHEIM⁽²⁾

$$\eta_j = \mu_j + z_j F \psi \quad \dots(1)$$

where μ_j is the chemical potential of the species j , z_j its valency (with sign included), F the Faraday and ψ the electrical potential of the phase to which η_j and μ_j relate.

In equilibrium the temperature and the electrochemical potentials of all the diffusible components are equal in the two phases, but the pressures may, and as a rule do, differ:

$$\eta_j^i = \eta_j^o \quad \dots(2)$$

where the two phases are distinguished by the superscripts i and o (inside and outside the membrane).

For ideal solutions these equalities can be written

$$\begin{aligned} \mu_j^s + p^i v_j + RT \ln x_j^i + z_j F \psi^i \\ = \mu_j^s + p^o v_j + RT \ln x_j^o + z_j F \psi^o \quad \dots (3) \end{aligned}$$

where it is assumed that the partial molar volume v_j of all components is independent of the pressure p . μ_j^s is the chemical potential in the standard state and x_j the mole fraction of species j .

The equations (3) together with the conditions for electro-neutrality (4) determine the state of the system completely.

$$\Sigma z_j x_j^i = 0 = \Sigma z_j x_j^o \quad \dots (4)$$

Specializing now for a completely dissociated uni-univalent salt, one non-diffusible (e.g. colloidal) ion of valency z and the solvent w , we obtain five equations

$$(p^i - p^o) v_+ + F(\psi^i - \psi^o) = RT \ln \frac{x_+^o}{x_+^i} \quad (5a)$$

$$(p^i - p^o) v_- - F(\psi^i - \psi^o) = RT \ln \frac{x_-^o}{x_-^i} \quad (5b)$$

.... (5)

$$(p^i - p^o) v_w = RT \ln \frac{x_w^o}{x_w^i} \quad (5c)$$

$$x_+^i - x_-^i + z x_z^i = 0 \quad x_+^o = x_-^o = x \quad (5d, e)$$

where the cation is indicated by +, the anion by -, the colloid ion by z and water by w .

The *distribution of ions* is found by adding eqs. (5a) and (5b)

$$\ln \frac{x_+^o x_-^o}{x_+^i x_-^i} = \frac{(p^i - p^o)(v_+ + v_-)}{RT} \quad \dots (6)$$

When the concentration of the colloid ion is not too large, the pressure difference $p^i - p^o$ is so small that the right-hand side of eq. (6) may be neglected.

The distribution of ions can then be calculated from eqs. (5d, e) and (7)

$$x_+^i x_-^i = x_+^o x_-^o \quad \dots (7)$$

or expressing in the same approximation the result in molar concentrations c instead of in mole fractions

$$c_+^i \cdot c_-^i = (c^o)^2 \quad \dots (8)$$

$$c_+^i - c_-^i + z c_z^i = 0 \quad \dots (9)$$

Here c^o is the salt concentration outside the membrane. The *osmotic pressure* follows easily from eq. (5c) in the following way

$$\begin{aligned}
 p^i - p^o &= \frac{RT}{v_w} \ln \frac{x_w^o}{x_w^i} = \frac{RT}{v_w} \ln \frac{1 - 2x}{1 - x_+^i - x_-^i - x_z^i} \\
 &\approx \frac{RT}{v_w} (x_+^i + x_-^i - 2x + x_z^i) \\
 &\approx RT(c_+^i + c_-^i - 2c^o + c_z^i) \quad \dots(10)
 \end{aligned}$$

which is simply Van't Hoff's expression.

The *potential difference* between the phases follows from eq. (5a) or (5b) after neglecting the small pv terms

$$\psi^i - \psi^o = \frac{RT}{F} \ln \frac{c_+^o}{c_+^i} = \frac{RT}{F} \ln \frac{c_-^i}{c_-^o} \quad \dots(11)$$

For comparison with approaches to be introduced later in this article, we shall give explicit equations for the extreme cases in which the colloid concentration is very much smaller or very much larger than the salt concentration viz. for $zc_z \ll c^o$ and for $zc_z \gg c^o$. (We drop the superscript i for the colloidal ion.)

Small colloid concentration

The solution of eqs. (8) and (9) including first order terms in $\frac{zc_z}{c^o}$ is

$$c_+^i = c^o - \frac{zc_z}{2} \quad \dots(12)$$

$$c_-^i = c^o + \frac{zc_z}{2} \quad \dots(13)$$

or, in words, *half of the charge of the non-diffusible ion is compensated by an excess of counterions and the other half by a shortage of the ions of the same sign as the colloid*, which we shall call the *co-ions*.

The osmotic pressure is equal to

$$p^i - p^o = RTc_z \quad \dots(14)$$

and the Donnan potential to

$$\psi^i - \psi^o = \frac{RT}{2F} \cdot \frac{zc_z}{c^o} \quad \dots(15)$$

The osmotic pressure has the same value as would be caused by the colloid ions alone.

Large colloid concentration

When $zc_z \gg c^o$, assuming that the colloid ion is positively charged we have

$$c_-^i = zc_z + \frac{(c^o)^2}{zc_z} \quad \dots(16)$$

$$c_+^i = \frac{(c^o)^2}{zc_z} \quad \dots(17)$$

The charge of the colloid ion is now nearly completely compensated by an excess of counterions.

The osmotic pressure is

$$p^i - p^o = RT(z + 1)c_z \quad \dots(18)$$

and thus not only the non-diffusible ions but also the counterions are osmotically active.

The Donnan potential is given by

$$\psi_i - \psi_o = \frac{RT}{F} \ln \frac{zc_z}{c^o} \quad \dots(19)$$

3. EQUILIBRIUM AND NON-EQUILIBRIUM PROPERTIES

A clear distinction should be maintained between the distribution of small ions and the osmotic pressure on one hand and the Donnan potential on the other hand. The first two are thermodynamically well-defined equilibrium properties.

The Donnan potential, however, can only be measured by introducing salt bridges into the two solutions and this adds irreversible processes to the equilibrium system. If, instead of using salt bridges, one would insert two identical reversible electrodes into the two solutions, zero potential difference would be found because the whole system would then be in equilibrium.

This fact, which has already been signalled by DONNAN and ALLMAND,⁽³⁾ is the basis of the so-called "indirect method" for determining the Donnan potential. LOEB^{(4), (5)} has remarked that the Donnan potential is equal to the difference in *pH* between the two phases multiplied by 58 mV and often preferred the two *pH* measurements on the separate liquids to the insertion of salt bridges into the equilibrium system. The principle of this method is illustrated in Fig. 1. If the four electrodes (two hydrogen electrodes, and two salt bridges with calomel electrodes) are inserted into the Donnan system there is no potential difference between the two reversible electrodes, because no work can be obtained from a system in equilibrium. Taking the common potential of these two electrodes as zero, the Donnan potential

THE DONNAN EQUILIBRIUM

is evidently equal to $E_1 - E_2$ and on the other hand E_1 and E_2 are the e.m.f.'s from which the respective pH 's are calculated. Consequently

$$pH_{\text{susp.}} - pH_{\text{equil. sol}} = \frac{E_{\text{susp.}} - E_{\text{equil. sol}}}{RT/0.4343F} \dots (20)$$

In soil and suspension chemistry this difference in pH (or in the logarithms of the activities of any other ion) between a suspension and its intermicellar liquid is known as the suspension effect (WIEGNER, PALLMANN^{(6), (7), (8)}). Recently its nature has formed the object of a

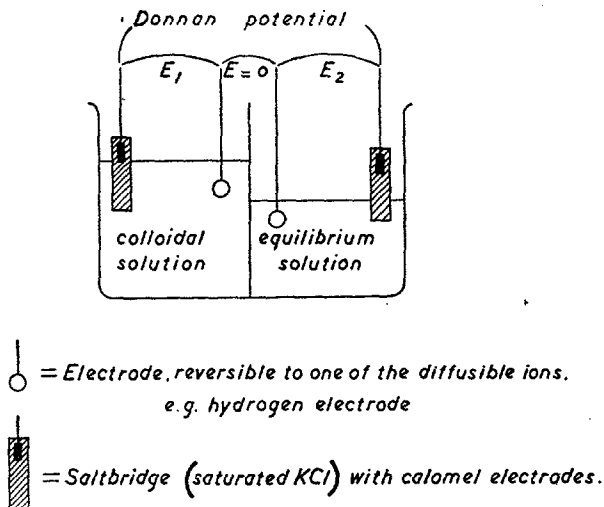


Fig. 1. Direct and indirect measurement of the Donnan potential. Demonstration of equality of Donnan potential and suspension effect.

rather heated discussion (JENNY *et al.*, MARSHALL, PEECH *et al.*, ERIKSSON, MYSELS, BABCOCK and OVERSTREET, SOLLNER, OVERBEEK, LOW⁽⁹⁻²⁰⁾).

It will be clear that any conclusion on the Donnan potential can be carried over immediately to the suspension effect and vice versa.

The Donnan potential has been defined as the potential difference between the two solutions. The assumption that the Donnan potential is equal to the potential difference between the two salt bridges, implies that the liquid junction potentials are zero or at least of equal magnitude. As no independent means of determining potential differences between phases of different composition exist, this assumption can never be checked. Even if this is a reasonable approach for dilute solutions of simple electrolytes, its application to suspensions containing highly charged colloidal particles is open to doubt.

When considering non-ideal Donnan systems, the distribution of ions and the osmotic pressure, although more difficult to calculate, still

remain equilibrium properties. In the case of the Donnan potential, however, a detailed consideration of the two irreversible liquid junctions will prove essential.

4. INTRODUCTION OF ACTIVITY COEFFICIENTS

In most cases Donnan equilibria do not obey the ideal laws. This is what we should expect considering that the non-diffusible ion is, as a rule, a highly charged colloidal particle which necessitates the introduction of large corrections for the deviations from ideal behaviour. These corrections can be given in the form of activity coefficients as has been done in a very rigorous way by DONNAN and GUGGENHEIM.⁽²¹⁾

Activity coefficients are introduced into equilibrium conditions of the type of eq. (3) by changing all x_j into $f_j \cdot x_j$ leading to:

$$\begin{aligned} \mu_j^s + p^i v_j + RT \ln f_j^i x_j^i + z_j F \psi^i \\ = \mu_j^s + p^o v_j + RT \ln f_j^o x_j^o + z_j F \psi^o \quad \dots (21) \end{aligned}$$

The condition of electroneutrality is unchanged

$$\sum z_j x_j^i = 0 = \sum z_j x_j^o \quad \dots (4)$$

Using the same treatment as in section 2, these conditions lead to the following equations.

For the distribution of ions we find instead of eq. (8):

$$f_+^i f_-^i c_+^i c_-^i = f_+^o f_-^o (c^o)^2 \quad \dots (22a)$$

$$\text{or} \quad (f_{\pm}^i)^2 c_+^i c_-^i = (f_{\pm}^o)^2 (c^o)^2 \quad \dots (22b)$$

The osmotic pressure is given by eq. (23), which replaces eq. (10):

$$p^i - p^o = \frac{RT}{v_w} \ln \frac{f_w^o x_w^o}{f_w^i x_w^i} = gRT(c_+^i + c_-^i - 2c^o + c_z^i) \quad \dots (23)$$

Here g is the conventional osmotic coefficient. Instead of eq. (11) the Donnan potential is given by:

$$\psi^i - \psi^o = \frac{RT}{F} \ln \frac{f_+^o c_+^o}{f_+^i c_+^i} \quad \dots (24)$$

Although the above equations are correct, they are of little practical value unless theoretical estimates for the activity coefficients can be given. An obvious approach for dilute systems is the use of Debye-Hückel activity coefficients. This has given satisfactory results in the case of the Donnan equilibrium $\text{KCl} - \text{K}_4\text{Fe}(\text{CN})_6$ with a membrane impermeable to the ferrocyanide ion. This system has been investigated by DONNAN and ALLMAND⁽³⁾ and by KAMEYAMA,⁽²²⁾ who

interpreted it with the help of LEWIS activity coefficients. HÜCKEL⁽²³⁾ showed that the results could also be explained with the help of Debye-Hückel activity coefficients. Quite recently, HILL⁽²⁴⁾ has shown that results equivalent to the use of Debye-Hückel coefficients are obtained by the application of the McMillan-Mayer theory of solutions, at least in the first approximation.

These theoretical approaches may be useful in the case of a relatively small non-diffusible ion or in the case of a swollen gel, where the fixed charges are distributed more or less uniformly. There are, however, serious drawbacks in the case of true polyelectrolytes where the non-diffusing charges are concentrated in a number of small spaces so that even with very great dilution of the polyelectrolyte molecules, the local concentration of ions remains high, close to the particle, and renders application of Debye-Hückel or similar theories impossible.

Instead of basing theoretical estimates of the activity coefficients on small departures of homogeneity as in the theory of DEBYE and HÜCKEL, a more promising approach is obtained by taking explicitly into account that the charges are concentrated in the colloidal particles. Such an approach has been given by DAVIS,⁽²⁵⁾ and more completely, by KLAARENBECK⁽²⁶⁾ and will be treated in the next section. A short account of KLAARENBECK's work has been given by the present author in KRUYT's *Colloid Science*.⁽²⁷⁾

5. APPROACH BASED UPON DETAILED CONSIDERATION OF THE UNEQUAL DISTRIBUTION OF IONS IN THE IONIC ATMOSPHERES

5.1 *Theory*

As mentioned in section 4, the application of the Debye-Hückel approximation to the Donnan equilibrium often fails, because, for the high concentrations of ions close to the colloidal particles the substitution of $(1 - e\psi/kT)$ for $\exp(-e\psi/kT)$, as used in the Debye-Hückel theory, is not valid*.

In the Gouy-Chapman theory of the electrical double layer, as applied in the theoretical treatment of the electrocapillary curve (GRAHAME⁽²⁸⁾), and in the theory of the stability of colloids (DERJAGUIN and LANDAU,⁽²⁹⁾ VERWEY and OVERBEEK⁽³⁰⁾), this approximation is not used but the full exponential is preserved. It is worth while to do the same for the Donnan equilibrium.

5.2. *Qualitative treatment for the distribution of ions*

In a Donnan equilibrium the counterions are concentrated in the inner solution, and the co-ions are driven away from it. In accordance with

* Here e is the ionic charge, ψ the local electrical potential, k BOLZMANN's constant and T the absolute temperature.

eq. (21) this is understood as a consequence of the equality of electrochemical potentials in the two phases. The difference in electrical potential ($\psi^i - \psi^o$) between the two phases entails a corresponding difference in the concentrations of all the diffusible ions. In eq. (21) it is implicitly assumed that the electrical potential may be considered as uniform in each of the two phases.

It is now proposed to take the variations of the electrical potential in different parts of the suspension into account. This amounts to applying eq. (21) locally to each volume element, instead of to the average of the whole inner or outer phase.

In other words, in the classical treatment the *average* concentration of ions is assumed to be related to the *average* electrical potential, whereas we are now relating the *local* concentrations to the *local* potentials, the averages being taken later.

The local concentrations, e.g. in the immediate neighbourhood of a colloidal particle, are given by the BOLTZMANN theorem.

$$c_+ = c^o \exp(-F\psi/RT); \quad c_- = c^o \exp(+F\psi/RT) \quad \dots (25)$$

where c_+ and c_- are the local concentrations of the cations and the anions respectively and ψ is the local potential. c^o is the concentration of ions in the outer solution. The BOLTZMANN expression (25) can be regarded as the solution of eq. (21) or rather of eq. (3) when the local activity coefficients are all equal and the small pv terms are neglected.

The average concentrations of ions are:

$$\bar{c}_{\pm} = c^o \overline{\exp(\mp F\psi/RT)} \quad \dots (26)$$

and this is only equal to the concentration calculated with the average potential

$$\bar{c}_{\pm}' = c^o \exp(\mp F\bar{\psi}/RT) \quad \dots (27)$$

when the electrical potential is everywhere small enough to permit the replacement of $\exp(x)$ by $(1+x)$.

If ψ is very small

$$\begin{aligned} \bar{c}_{\pm} &= c^o \overline{\exp(\mp F\psi/RT)} = c^o \overline{(1 \mp F\psi/RT)} \\ &= c^o (1 \mp F\bar{\psi}/RT) = c^o \exp(\mp F\bar{\psi}/RT) \quad \dots (28) \end{aligned}$$

If, however, the potential is high in the neighbourhood of the colloidal particles—and this occurs when the particles are highly charged and the ionic strength is low—then the accumulation of counterions is larger and the expulsion of co-ions smaller than corresponds to eq. (28). As the high potential close to the particles is nearly independent of the particle concentration, this dissymmetry persists *even in the case of very*

small colloid concentration, whereas according to the classical treatment the excess of counterions and the deficit of co-ions are the more nearly equal the lower the colloid concentration (cf. section 2). Fig. 2 illustrates the two cases.

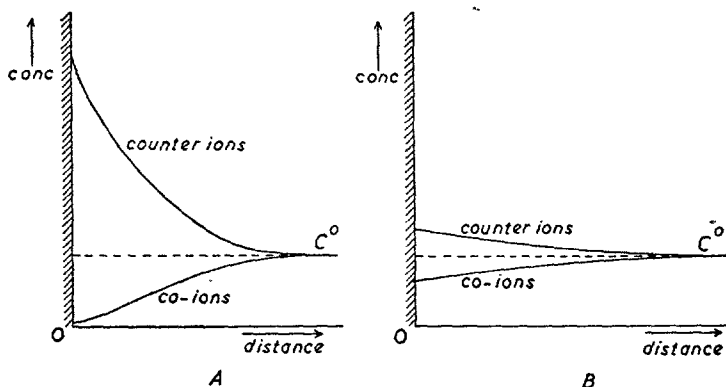


Fig. 2. Distribution of ions in the field of an electrically charged particle. A: for high potentials ($F\psi/RT > 1$). B: for low potentials ($F\psi/RT \ll 1$).

5.3. Qualitative treatment of osmotic pressure

In the classical treatment the osmotic pressure is determined by $c_+ + c_- - 2c^o + c_2$. When the inhomogeneity in the ionic concentrations is considered as in the foregoing subsection, one should consider that the pressure varies with the distance from the colloidal particles, the pressure being highest near the particles and lowest in certain

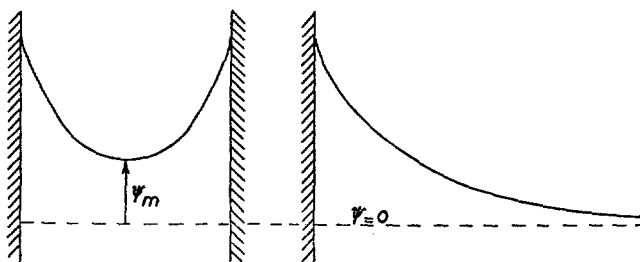


Fig. 3. Schematic representation of the course of the potential between two particles.

symmetry points midway between the particles. Eq. (3) or (5c) but now applied locally, allow the pressure to be calculated. The high pressures are partially counteracted by the stresses in the electric field and only in the symmetry point where the field strength is zero, may the pressure be considered as an osmotic pressure. In these symmetry points the potential still has a finite value (ψ_m) as shown schematically in Fig. 3. The pressure can then simply be calculated by

Van't Hoff's expression, which can be transformed with the aid of BOLTZMANN's theorem.

$$p^m - p^o = RT(c_+^m + c_-^m - 2c^o) \\ = RTc^o \{ \exp(F\psi_m/RT) + \exp(-F\psi_m/RT) - 2 \} \dots (29)$$

where the index m stands for the symmetry points.

The osmotic pressure (rather, the contribution of the diffusible ions to the osmotic pressure) should be found by averaging expression (29) over all possible configurations. If the particles are not highly charged, so that mutual repulsion may be neglected, this averaging should lead to the classical value for the contribution of the small ions to the osmotic pressure

$$\bar{p} - p^o = RTc^o \{ \exp(F\bar{\psi}/RT) + \exp(-F\bar{\psi}/RT) - 2 \} \dots (30)$$

If, however, the charges are high, the particles repel each other and approach a more lattice-like arrangement where the mutual distances are more or less identical and all p_m 's are about equal, eq. (29) immediately giving the ionic contribution to the osmotic pressure.

As ψ_m in this regular arrangement is evidently smaller than the average value of the potential, the actual osmotic pressure is lower than the one calculated from average ionic concentrations. Experimentally this fact is known as the HAMMARSTEN effect.^{(31), (32)}

5.4. Quantitative treatment of the distribution of ions

In order to give an accurate quantitative treatment based on the above ideas it would be necessary to take account of form, size and geometrical arrangement of the colloidal particles. As this is evidently beyond our actual powers of calculation, some approximation in this respect is necessary, but it is essential to conserve the possibility of using high values of the electrical potential. The most extensive treatment of the ionic atmospheres in the case of high potentials has been given for large flat faces. We follow therefore KLAARENBEEK'S^{(26), (27)} idea of representing the particles in a Donnan equilibrium as bounded by flat faces, neglecting any end effects.

In the first place we shall treat solutions, which are very dilute with respect to the colloidal particles, so that overlapping of double layers can be neglected. In this case the relative differences in the concentrations of ions in the two phases are very small. Instead of describing the distribution of ions by the ratio of the concentrations in the two phases, it can be more conveniently expressed as the fraction of the charge of the colloid that is compensated by an excess of counterions or by a deficit of co-ions respectively. This excess and deficit can be found by integrating the local concentrations over the available volume

and subtracting the bulk concentration taken over the same volume. The total charge is found as the sum of deficit and excess.

Consequently the fraction of the charge compensated by an excess of counterions, α_+ , is equal to

$$\alpha_+ = \frac{\int_0^\infty [\exp(-F\psi/RT) - 1] dx}{\int_0^\infty [\exp(-F\psi/RT) - \exp(F\psi/RT)] dx} \dots (31)$$

and similarly the fraction compensated by a deficit of co-ions, α_- , is given by

$$\alpha_- = \frac{\int_0^\infty [1 - \exp(F\psi/RT)] dx}{\int_0^\infty [\exp(-F\psi/RT) - \exp(F\psi/RT)] dx} \dots (32)$$

where x represents the distance from the plane face of the particle. The particles are considered to be negatively charged and consequently ψ is always negative.

The integrations are straightforward and relatively simple when it is assumed that the electrical double layer is of the GOUY-CHAPMAN type^{(33), (34)} (cf. VERWEY and OVERBEEK⁽³⁰⁾).

The distribution of charges in the double layer obeys the Poisson-Boltzmann equation

$$\frac{d^2\psi}{dx^2} = \frac{4\pi Fc}{\epsilon} [\exp(F\psi/RT) - \exp(-F\psi/RT)] \dots (33)$$

where c is the electrolyte concentration far from the particles and ϵ the dielectric constant of the solution.

A first integration leads to

$$\frac{d\psi}{dx} = -\sqrt{\frac{8\pi cRT}{\epsilon}} [\exp(F\psi/2RT) - \exp(-F\psi/2RT)] \dots (34)$$

where the fact that $d\psi/dx = 0$ at infinity has been taken into account. The proportionality between the surface charge density σ , and the field strength as given in eq. (35)

$$\sigma = -\frac{\epsilon}{4\pi} \left(\frac{d\psi}{dx} \right)_{\text{surface}} \dots (35)$$

leads to a simple relation between surface charge σ , and surface potential ψ .

$$\sigma = \sqrt{\frac{ecRT}{2\pi}} [\exp(F\psi_0/2RT) - \exp(-F\psi_0/2RT)] \dots (36)$$

where ψ_0 is the potential at the surface of the particle, i.e. at $x = 0$ while the potential is assumed to be zero at infinity.

The integral in eq. (32) for the co-ions can be transformed as follows:

$$\int_0^\infty [1 - \exp(F\psi/RT)] dx = \int_{\psi_0}^0 \frac{[1 - \exp(F\psi/RT)]}{d\psi/dx} d\psi \dots (37)$$

UNEQUAL DISTRIBUTION OF IONS IN IONIC ATMOSPHERES

Substituting $d\psi/dx$ from eq. (34) we find

$$\int_{\psi_0}^0 \frac{[1 - \exp(F\psi/RT)]}{d\psi/dx} d\psi = \sqrt{\frac{\epsilon}{8\pi cRT}} \int_0^{\psi_0} \frac{1 - \exp(F\psi/RT)}{\exp(F\psi/2RT) - \exp(-F\psi/2RT)} d\psi$$

$$= -\sqrt{\frac{\epsilon}{8\pi cRT}} \int_0^{\psi_0} \exp(F\psi/2RT) d\psi = \sqrt{\frac{\epsilon RT}{2\pi cF^2}} [1 - \exp(F\psi_0/2RT)] \dots (38)$$

The integral in the denominator is handled similarly, leading to

$$\int_0^{\infty} [\exp(-F\psi/RT) - \exp(F\psi/RT)] dx$$

$$= \sqrt{\frac{\epsilon RT}{2\pi cF^2}} [\exp(-F\psi_0/2RT) - \exp(F\psi_0/2RT)] \dots (39)$$

The fraction of the particle charge compensated by a deficit of co-ions is thus

$$\alpha_- = \frac{\exp(F\psi_0/2RT) - 1}{\exp(F\psi_0/2RT) - \exp(-F\psi_0/2RT)} \dots (40)$$

For very small values of the surface potential this fraction is equal to $\frac{1}{2}$ in agreement with Fig. 2B, but for larger values of ψ_0 , i.e. for more highly charged particles, it decreases as shown in Table 1.

TABLE I

Fraction of α_- ions expelled (α_-) as related to the surface potential ψ_0

$\frac{F\psi_0}{RT}$	ψ_0^* in millivolts	α_-
0	0	0.50
1	25	0.38
2	50	0.27
4	100	0.12
8	200	0.018

* At room temperature, $\frac{RT}{F}$ is close to 25 millivolt.

According to the elementary theory treated in par. 2 the fraction always goes to $\frac{1}{2}$ when the colloid concentration is lowered sufficiently (cf. eqs. 12, 13). In the present treatment the distribution remains asymmetrical, even at very high dilution.

5.5 Higher concentrations of the non-diffusible ions

Considering now higher particle concentrations where the double layers overlap significantly, we have to treat the case of two flat parallel faces carrying double layers as pictured in Fig. 3.

The overlapping of the double layers obviously makes the absolute value of the potential higher and cuts off the low potential tail of the double layer. Consequently the average values of $\exp(\mp F\psi/RT)$ become more extreme and the fraction of the particle charge compensated by the counterions will be larger, that compensated by the co-ions smaller. Qualitatively, the change is in the same direction as in the classical treatment; quantitatively it is less pronounced, because considerable interaction of double layers with high surface potentials is necessary before significant changes in the distribution of ions occur.

For a quantitative treatment we start again from the Poisson-Boltzmann equation (33). A first integration now leads to

$$\frac{d\psi}{dx} = -\sqrt{\frac{8\pi cRT}{\epsilon}} \sqrt{2 \cosh F\psi/RT - 2 \cosh F\psi_m/RT} \quad \dots (41)$$

where the boundary condition $\frac{d\psi}{dx} = 0$ half-way between the plates has been used.

The total counter charge ($-\sigma$) per cm^2 of the double layer in one-half of the space between the two particles is given by

$$-\sigma = \frac{\epsilon}{4\pi} \left(\frac{d\psi}{dx}\right)_{\text{surface}} = \sqrt{\frac{\epsilon cRT}{2\pi}} \sqrt{2 \cosh F\psi_0/RT - 2 \cosh F\psi_m/RT} \quad \dots (42)$$

The part of the total counter charge formed by the expulsion of co-ions can be written

$$\alpha_- = -\frac{Fc}{\sigma} \int_0^d (1 - \exp F\psi/RT) dx \quad \dots (43)$$

After substituting $\frac{d\psi}{d\psi/dx}$ for dx this integral can be transformed into:

$$\alpha_- = \frac{1}{\sigma} \sqrt{\frac{\epsilon cRT}{8\pi}} \int_{F\psi_0/RT}^{F\psi_m/RT} \frac{e^y - 1}{\sqrt{2 \cosh y - 2 \cosh (F\psi_m/RT)}} dy \quad \dots (44)$$

The solution of the integral can be given with the aid of elliptic integrals, leading to

$$\alpha_- = \frac{[(E(e^a, \pi/2) - E(e^a, \arcsin e^{\frac{z-a}{2}}))] - (1 - e^a)[F(e^a, \pi/2) - F(e^a, \arcsin e^{\frac{z-a}{2}})]}{e^{a/2} \sqrt{e^{2z} + e^{-2z} - e^a - e^{-a}}} \quad \dots (45)$$

where $a = F\psi_m/RT$, $z = F\psi_0/RT$, $F(k, \phi)$ is an elliptic integral of the first kind and $E(k, \phi)$ is an elliptic integral of the second kind in the notation of JAHNKE and EMDE.⁽³⁵⁾

An application of these relations to the Donnan equilibrium demands the knowledge of ψ_m and ψ_0 . These potentials are related through the charge density as expressed in eq. (42). If we assume the charge density to be a given quantity, one further relation is necessary. In principle this relation can be derived from the concentration of the colloid. This determines the distance $2d$ between the plates, and by a second integration of eq. (41) a relation between ψ_0 , ψ_m and $2d$ can be established. However, KLAARENBECK⁽²⁶⁾ felt that this might stretch the rather rough model too far and he therefore derived ψ_m from the experimentally determined osmotic pressure.

Eq. (46) shows how ψ_m is related to the osmotic pressure (cf. eq. 92).

$$p - p^o = RTc^o [\exp (F\psi_m/RT) + \exp (- F\psi_m/RT) - 2] \dots (46)$$

With ψ_m and σ known, ψ_o can be calculated from eq. (42) and all the data necessary to evaluate α_- are given.

5.6. Strong interaction of double layers

If the particles come very close together the potential drop between ψ_o and ψ_m becomes smaller and smaller as illustrated in Fig. 4. This means that the local concentrations of ions are not very variable and that we are again back at the classical Donnan situation, where distribution of ions, osmotic pressure and Donnan potential are simply

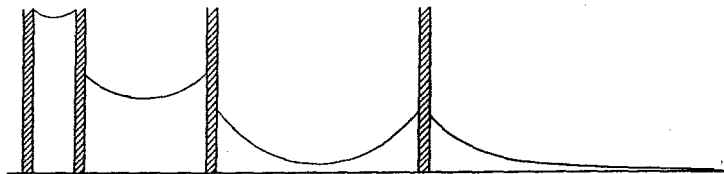


Fig. 4. Illustrating schematically that the range of potentials between two particles becomes relatively smaller, the closer the particles are together.

given by the elementary equations as treated in section 2. It is remarkable that the new treatment of the Donnan effects may deviate strongly from the classical treatment when the colloid concentration is low, but not when it is high.

5.7. Activity coefficients

It would be possible to calculate activity coefficients corresponding to the treatment given in this section, but such a calculation would have no great advantages. Activity coefficients are introduced in order to give account of deviations of classical laws. They are strictly empirical quantities. As soon as a theoretical explanation is put forward the introduction of activity coefficients does not throw any fresh light on the problem.

5.8. Experimental data

The theoretical picture outlined in the preceding sections, has been drawn in order to explain a number of deviations from ideal behaviour. Of the existing experimental data, those of KLAARENBECK⁽²⁶⁾ on the Donnan equilibrium of gum arabic with KBr are best suited to test the theory and to show its advantages over the classical approach.

KLAARENBECK used solutions of Na arabinat⁽²⁶⁾ with a molecular weight of about 200,000 and an equivalent weight of 1180. Potassium bromide was used as the diffusible salt because the Br⁻ ion can be

THE DONNAN EQUILIBRIUM

determined relatively easily. KLAARENBECK determined the distribution of ions by measuring the Br^- content inside and outside the membrane, the osmotic pressure and in a number of cases the Donnan potential. His results on the distribution of ions can be most easily expressed as the amount of Br^- expelled: cf. eq. (40).

The drawn curves in Fig. 5 are experimentally determined lines. The dotted lines are valid for ideal behaviour or for equal mean activity coefficients in the two phases. It is seen that, especially at the lower concentrations of KBr, the deviations are striking. They do not disappear with diminishing concentrations of gum arabic. This fact, that even at very high dilution of the colloidal particles the Donnan theory for ideal behaviour is not followed, is one of the strongest indications of the necessity of considering a dilute solution of a colloid as a number of islands of high concentration of ions dispersed in a solution of a much lower concentration, rather than as a completely homogeneous system.

The experimental slopes at zero gum arabic concentration in 0.001, 0.01, 0.1 and 1 N KBr solutions are 0.11; 0.19; 0.32 and 0.50 g eq. Br^- expelled per g eq. gum respectively.

Using eq. (40), these slopes allow the calculation of the surface potential and with the aid of eq. (36), of the apparent surface charge density.

TABLE 2
Surface Potential and Surface Charge Density of the Gum Arabic Particles as calculated from the Distribution of Ions

<i>Conc. of KBr in g eq. per litre</i>	<i>g eq. Br^- expelled per g eq. gum arabic</i>	<i>Surface potential ψ_0 in mV</i>	<i>Surface charge density σ in e.s.u. per cm^2</i>
0.00108	0.115	102	- 4300
0.01	0.19	72	- 7100
0.1	0.32	37	- 8700
1.0	0.50	(0)	(0)

The order of magnitude of potential and charge density is not unreasonable; neither is the fact that the potential decreases and that the charge density increases with decreasing concentration of salt (the value 0 for σ at the highest salt concentration is extremely sensitive to error in the analytical determination).

Considering for a moment the gum arabic molecule (M.W. 220,000, Equiv. W. 1180) as a spherical particle with 185 elementary charges, a charge density of 7000 e.s.u./ cm^2 would correspond to a surface area of 1.3×10^{-11} or a radius of 10^{-6} cm, which is quite a reasonable figure,

UNEQUAL DISTRIBUTION OF IONS IN IONIC ATMOSPHERES

corresponding well with a value of 1.1×10^{-6} cm from diffusion (BRUINS⁽³⁷⁾) and of about 10^{-6} cm from titration curves (OVERBEEK⁽³⁸⁾).

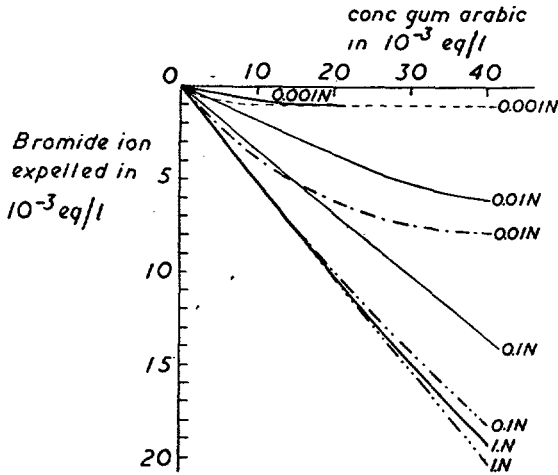


Fig. 5. Expulsion of Br^- ions in the Donnan equilibrium between gum arabic and KBr for four different concentrations of the outside solution. The experimental curves are drawn. The dotted curves represent ideal behaviour.

The curves for 1 N and 0.1 N KBr are practically straight lines, indicating the absence of measurable overlapping of double layers.

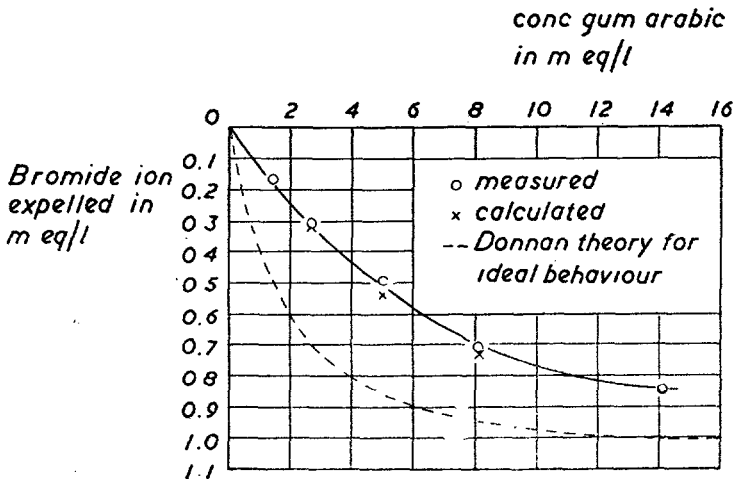


Fig. 6. Expulsion of Br^- ions from solutions of gum arabic with 0.00108 N KBr, as measured (o), calculated from eq. (45) (x), and calculated for ideal behaviour (dotted line).

The curvature of the 0.01 N and 0.001 N lines indicates that at higher concentrations of gum arabic some interaction of the double layers can

THE DONNAN EQUILIBRIUM

be detected, resulting in a still smaller expulsion of co-ions. Quantitatively this should be explained by the theory as indicated in section 5.5. It has been mentioned there already that given the difference between the model (flat faces) and the actual situation (coiled molecules), a straightforward calculation of the effect of higher concentrations of the colloid is hardly possible. KLAARENBEEK has therefore calculated the value of the potential half-way between the plates, from the osmotic pressure with the aid of eq. (46), and assuming a surface potential independent of the concentration of gum he has calculated the amount of co-ions expelled. Numerical data are given in Table 3 and shown for 0.001 N KBr in Fig. 6. The good agreement between calculated and experimental values is another indication that although the model may be rough the line of thought indicated in this section merits serious consideration.

TABLE 3
Experimental and Calculated Values for the Expulsion of Co-ions at Higher Concentrations of Gum Arabic

Conc. KBr	Eq. conc. gum arabic	Osmotic pressure in cm H ₂ O	Potential half way in mV calculated with eq. (46)	Surface potential in mV (from Table 2)	Br ⁻ ion expelled in g eq. per g eq. gum arabic	
					Calculated from eq. (45)	Found
0.00108 N	1.4 × 10 ⁻³ N	0.3	2.8	102	0.119	0.118
"	2.7 "	1.9	6.8	"	0.116	0.113
"	2.0 "	8.7	14.6	"	0.108	0.099
"	8.1 "	32.9	27.7	"	0.090	0.087
"	14.1 "	12.7	39.2	"	0.071	0.060
0.01 N	2.7 ⁶ × 10 ⁻³ N	1.35	1.8	72	0.197	0.17
"	5.5 "	2.1	2.2	"	0.195	0.193
"	11.0 "	6.5	4.0	"	0.194	0.192
"	20.3 "	23.8	7.8	"	0.189	0.181
"	30 "	74.1	13.6	"	0.176	0.170

6. THE DONNAN POTENTIAL

6.1. *On the location of the Donnan potential*

It has already been mentioned in section 3, that the Donnan potential and the e.m.f. connected with the suspension effect are identical, and that saturated KCl bridges play an important role in their measurement. In the usual interpretation of this measurement the liquid junctions with saturated KCl are assumed to be potential free, or nearly so, the measured e.m.f. being located nearly exclusively at, or in the membrane between the two Donnan phases. It is, however, by no means certain

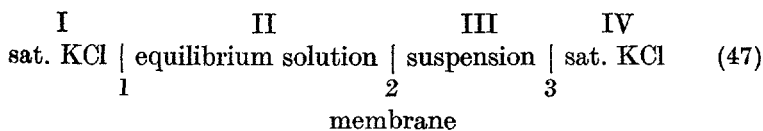
that the diffusion potential between saturated KCl and a colloidal solution or a suspension is small. In a liquid junction between saturated KCl and a dilute solution of electrolytes of low molecular weight, the contribution to the diffusion potential of the concentration gradient of the dilute electrolyte is negligible, because it is drowned in a large excess of KCl. The concentration gradient of the KCl does not contribute to the diffusion potential because the mobilities of K^+ and Cl^- are nearly the same. In the liquid junction between saturated KCl and a colloidal solution or suspension, the diffusion gradient of the colloid still plays a negligible part on account of the high excess of KCl. In the tail of the concentration gradient of KCl, however, where the equivalent concentration of KCl is of the same order as that of the colloidal ions, the mobilities of K^+ and Cl^- may be considerably changed in the high electric fields around the particles. The changes for K^+ and Cl^- are in opposite directions and thus may lead to a considerable diffusion potential. It has even been argued by JENNY *et al.*⁽⁹⁾ and by BABCOCK and OVERSTREET,⁽¹⁷⁾ that the Donnan potential is completely situated at this liquid junction and not at the membrane. However, we run up here against the well-known difficulty of defining the potential difference between two phases of different composition. GUGGENHEIM^{(39), (40)} showed that this quantity is not accessible to any experimental determination.

There is a way out of this difficulty, as a theory can be formulated on the e.m.f. of the complete Donnan cell (including the two liquid junctions) in which these equivocal potentials of separate phases are avoided (OVERBEEK⁽¹⁹⁾).

It has been proposed that this e.m.f. which is accessible to measurement, be called the Donnan e.m.f., as distinct from the Donnan potential between the two phases, which cannot be measured.

4.2. Formulation of the Donnan e.m.f.

The essential part of the cell with the aid of which the Donnan e.m.f. is usually determined, consists of the two Donnan phases in equilibrium, each in contact with a saturated solution of KCl. It is irrelevant to which type of reversible



electrodes the saturated KCl phases are connected. The membrane is permeable to water and to all the small ions and supposedly, completely impermeable to the suspended particles.

The total e.m.f. of the cell⁽⁴⁷⁾ can be calculated as the sum of three

liquid junction potentials. Applying the usual equation for the *l.j.* potential (cf. MACINNES⁽⁴¹⁾) one finds

$$-EF = \int_{\text{left}}^{\text{right}} \sum_i \frac{t_i}{z_i} d\mu_i \quad \dots (48)$$

where the sum is to be taken over all the ions, including the colloidal particles. t_i is the transference number, z_i the valence with sign included, and μ_i the chemical potential of the species i . In order to transform the chemical potentials of single ions occurring in (48), into chemical potentials of neutral systems, we add to (48) the obvious equality (49).

$$0 = \int_{\text{left}}^{\text{right}} \sum_i t_i d\mu_K \quad \dots (49)$$

where K represents a monovalent positive reference ion, say the potassium ion.

The integral in (49) is zero because $\sum t_i = 1$ and μ_K has the same value in the two saturated KCl solutions.

In this way we find

$$-EF = \int_{\text{left}}^{\text{right}} \sum_i t_i \left(\frac{d\mu_i}{z_i} - d\mu_K \right) \quad \dots (50)$$

The expression in parentheses refers to a neutral substance. If i represents a negative ion,

$$\frac{d\mu_i}{z_i} - d\mu_K = \frac{1}{z_i} (d\mu_i - z_i d\mu_K) = \frac{1}{z_i} d\mu_{K_i}$$

where K_i is the salt consisting of one i -ion and z K^+ -ions. If i is a positive ion $\frac{d\mu_i}{z_i} - d\mu_K$ represents the change in free energy accompanying an ion exchange of one K -ion by $1/z_i$ i -ion.

Eq. (50) can be further transformed by splitting the integral into three integrals relating to the three phase boundaries in the cell (47).

$$\begin{aligned} -EF = & \int_{\text{sat. KCl}}^{\text{equil. sol}} \sum_i t_i \left(\frac{d\mu_i}{z_i} - d\mu_K \right) + \int_{\text{equil. sol}}^{\text{suspension}} \sum_i t_i \left(\frac{d\mu_i}{z_i} - d\mu_K \right) \\ & + \int_{\text{suspension}}^{\text{sat. KCl}} \sum_i t_i \left(\frac{d\mu_i}{z_i} - d\mu_K \right) \quad \dots (51) \end{aligned}$$

As the two Donnan phases are in equilibrium, the chemical potentials of all diffusible salts are equal in these two phases. The chemical potential of a salt of which the non-diffusible ions form a component, changes across the membrane but the transference number of the non-diffusible ions is obviously zero in the membrane. Consequently all the

terms in the sum in the second integral of eq. (51) are zero and the equation for the Donnan e.m.f. reduces to

$$-EF = \int_{\text{sat. KCl}}^{\text{equil. sol}} \sum_i t_i \left(\frac{d\mu_i}{z_i} - d\mu_K \right) + \int_{\text{suspension}}^{\text{sat. KCl}} \sum_i t_i \left(\frac{d\mu_i}{z_i} - d\mu_K \right) \dots (52)$$

This equation which has a clear thermodynamic significance, not only shows that the e.m.f. of the Donnan cell can be completely expressed in the properties of the solutions at the two liquid junctions, but also that this e.m.f. is connected with transference numbers as well as with chemical potentials.

In order to evaluate the Donnan e.m.f. in practical cases, the relations between transference numbers and chemical potentials in the liquid junctions have to be ascertained. Although strictly, the course of the concentrations of all the components in the liquid junctions has to be known, a very reasonable approximation is obtained by assuming that in the significant part of the *l.j.* the colloidal particles and all the other constituents of the Donnan system have a constant concentration, the only variation being a gradient of the concentration of potassium chloride.

6.2.1. Ideal solutions

If all the solutes, including the non-diffusible ions, behave ideally both with respect to mobility and to activity, the following relations hold.

$$\left. \begin{aligned} \sum_{i \neq K, Cl} t_i &= 1 - t_K - t_{Cl} \\ d\mu_i &= RT \frac{dc_i}{c_i}; d\mu_K = RT \frac{dc_K}{c_K} \\ dc_K &= dc_{Cl} \end{aligned} \right\} \dots (53)$$

Substituting the relations (53) into eq. (52) leads to:

$$\begin{aligned} -EF &= \int_{\text{sat. KCl}}^{\text{equil. sol}} (1 - t_K - t_{Cl})(-d\mu_K) + t_{Cl}(-d\mu_{Cl} - d\mu_K) \\ &\quad + \text{similar expression for the second integral} \\ &= -EF = RT \int_{\text{sat. KCl}}^{\text{equil. sol}} \left(-\frac{dc_K}{c_K} + \frac{t_K dc_K}{c_K} - \frac{t_{Cl} dc_{Cl}}{c_{Cl}} \right) \\ &\quad + RT \int_{\text{suspension}}^{\text{sat. KCl}} \left(-\frac{dc_K}{c_K} + \frac{t_K dc_K}{c_K} - \frac{t_{Cl} dc_{Cl}}{c_{Cl}} \right) \\ &= -EF = RT \int_{\text{sat. KCl}}^{\text{equil. sol}} \left[\left(\frac{t_K}{c_K} - \frac{t_{Cl}}{c_{Cl}} \right) dc_K - d \ln c_K \right] \\ &\quad + RT \int_{\text{suspension}}^{\text{sat. KCl}} \left[\left(\frac{t_K}{c_K} - \frac{t_{Cl}}{c_{Cl}} \right) dc_K - d \ln c_K \right] \end{aligned}$$

As the mobilities of K^+ and Cl^- are very nearly equal, the transference numbers of these ions are in nearly the same ratio as their concentration. Thus the terms $(t_K/c_K - t_{Cl}/c_{Cl})$ are very close to zero and the Donnan e.m.f. reduces to

$$E = \frac{RT}{F} \left[\int_{\text{sat. KCl}}^{\text{equil. sol.}} d \ln c_K + \int_{\text{suspension}}^{\text{sat. KCl}} d \ln c_K \right] = \frac{RT}{F} \ln \frac{c_K \text{ equil. sol.}}{c_K \text{ suspension}} \dots (54)$$

which is identical to eq. (11). This shows that the treatment *via* the liquid junction potentials is equivalent to the classical treatment, provided the approximations for ideal behaviour are used.

6.2.2. Deviations from ideal behaviour

In order to apply eq. (52) to non-ideal cases, both transference numbers and chemical potentials have to be known as functions of the composition of the solutions in the liquid junctions. In the present state of our knowledge of these quantities, the best we can do is to use a very simple example, i.e. a solution of a potassium salt of a polyelectrolyte ion P with valence z and potassium chloride, and make reasonable estimates of mobilities and activities.

Specializing eq. (52) to the case just mentioned one obtains:

$$E_{\text{Donnan}} = \frac{1}{F} \int_{\text{sat. KCl}}^{\text{equil. sol.}} t_{Cl} d\mu_{KCl} + \frac{1}{F} \int_{\text{suspension}}^{\text{sat. KCl}} \left(t_{Cl} d\mu_{KCl} + \frac{t_P}{z} d\mu_{PK.} \right) \dots (55)$$

The term $\frac{t_P}{z} d\mu_{PK.}$ is usually small. We will neglect its influence here, but if wanted it can be expressed in terms of $d\mu_{KCl}$ and the composition of the system as has been shown by OVERBEEK.⁽¹⁹⁾ In the two integrals μ_{KCl} has the same limits. Eq. (55) can thus be written

$$E_{\text{Donnan}} = \frac{1}{F} \int_{\mu_o}^{\text{sat. KCl}} (t_{Cl(\text{susp.})} - t_{Cl(\text{equil. sol.})}) d\mu_{KCl} \dots (56)$$

in which μ_o is the chemical potential of KCl in suspension and equilibrium solution.

Assuming the mobilities of K^+ and Cl^- to be equal the transference number in the equilibrium solution is $\frac{1}{2}$. In the suspension the transference number differs from $\frac{1}{2}$ for two reasons. In the first place there are more K^+ ions than Cl^- ions (we neglect here the contribution to the conduction by the non-diffusible ions). In the second place the mobilities of K^+ and Cl^- in the neighbourhood of the colloidal particles are modified. Especially the mobility of the counterions may be far below their normal value as is proved by the low equivalent conductivity

THE DONNAN POTENTIAL

of completely dialyzed suspensions or polyelectrolyte solutions. A reduction of the mobility by a factor four is not exceptional.^{(19), (42)} The mobility of the co-ions will not be greatly changed because they are driven away from the regions of high charge density.

If the non-diffusible ions carry a high charge (and this is the case when deviations from ideal behaviour will be most obvious), it will not be a bad approximation to assume that this charge is completely compensated by an excess of counterions, the concentration of co-ions remaining the same as in the equilibrium solution (cf. section 5.4). Assuming moreover that the mobility of the co-ions is completely unaffected and that the mobility of the counterions compensating the charge of the non-diffusible particles is reduced to $1/r$ of its normal value, the transference number of the Cl ion in the suspension is given by

$$t_{Cl} = \frac{c}{2c + zc_z \frac{1}{r}} \quad \dots(57)$$

where c is the concentration of KCl in equilibrium with the suspension and c_z is the molar concentration of particles.

Writing $2RT d \ln c$ for $d\mu_{KCl}$, eq. (56) is now easily integrated leading to

$$E_{\text{Donnan}} = \frac{RT}{F} \ln \frac{c}{c + \frac{zc_z}{2r}} \quad \dots(58)$$

For a dilute suspension this is approximately equal to

$$E_{\text{Donnan}} = - \frac{RT}{2F} \cdot \frac{zc_z}{c} \cdot \frac{1}{r} \quad \dots(59)$$

This expression, being identical to the ideal expression (15) except for the factor $1/r$ shows that the first and biggest effect on the Donnan e.m.f. is given by the non-ideal behaviour of the mobilities rather than of the activities.

6.3. *Experimental evidence*

A complete test of the theoretical considerations given in this section cannot yet be given because the necessary transference data are lacking. We can only take some existing data on Donnan-potentials and compare interpretations with the theory just described and with the classical Donnan approach.

KLAARENBEEK⁽²⁶⁾ determined Donnan e.m.f.'s in systems containing sodium arabinatate and KBr. The e.m.f. was proportional to the concentration of gum, with proportionality constants of 3.5, 0.7 and

0.07* mV per milli equivalent of gum for KBr equilibrium concentrations of 0.001, 0.01 and 0.1* *N* respectively. In a 1 *N* solution there was no measurable e.m.f. Interpretation of these data with the classical equation

$$E = \frac{RT}{2F} \frac{zc_z}{c^0} \dots (15)$$

would lead to the conclusion that the degree of dissociation of Na (or K) arabinates is equal to 30 per cent, 60 per cent and 60 per cent* in 0.001, 0.01 and 0.1 *N* KBr respectively. It does not seem reasonable to suppose that the dissociation should *increase* with increasing content of salt. The interpretation with eq. (52) or approximately with eq. (59) would mean that in the lower electrolyte concentration the mobility of the cations is considerably decreased and this is wholly in line with the fact that at low ionic strengths the electrical potential around the particles is high.

Similar conclusions can be drawn from data on the Donnan e.m.f. of sodium bentonite published by DAVIS⁽²⁵⁾ in which the apparent degree of dissociation increases from 2.5 per cent to 10 per cent when the NaCl concentration increases from 0.001 to 0.01 *N*.

ADAIR and ADAIR^{(43), (44), (45)} made very careful and highly accurate measurements of the Donnan e.m.f. of a number of protein systems and of Congo red. In all cases they found a linear relationship between concentration of colloid and e.m.f. provided that the latter was not more than a few millivolts. They considered this as suggesting that the activity coefficients of the diffusible salts are the same in the two phases and therefore as an indication of the applicability of eq. (15). We have seen, however, that the linearity by itself is a consequence of either theory. It is therefore desirable to compare the valence of the colloid as calculated with eq. (15) with independent evidence. Measurements on Congo red,⁽⁴³⁾ a disodium salt of a disulphonic acid which is aggregated in solution, interpreted with eq. (15) seem to show that only 50 per cent of the sodium ions are dissociated. Unfortunately the data are given for one ionic strength (0.02) only, so that the course of this degree of dissociation with concentration of salt is not known. However, the assumption that the mobility of the sodium counterions is decreased by 50 per cent seems preferable to the assumption of a very incomplete dissociation of a sodium salt of a sulphonic acid in dilute solution (0.02 M).

ADAIR's data on protein, viz. edestin, serum albumin, hemoglobin⁽⁴³⁾ and egg albumin⁽⁴⁵⁾ and the recent data by CHARLWOOD⁽⁴⁶⁾ on horse serum albumin all show a relatively good agreement of the valence of these proteins calculated from eq. (15) with independent estimates of the valence, e.g. from analytical data, from osmotic pressures and from

* The figures for the 0.1 *N* solution are rather uncertain because *E* is so small.

electrophoretic mobilities.^{(46), (47)} As most of these experiments have been performed at relatively high ionic strengths, the electrical potentials in the ionic atmospheres were rather low, which explains the good agreement. Larger deviations from the classical theory are expected especially for low salt contents.

A remarkable effect that has been observed in studies on the suspension effect in clays^{(14), (48)} is a reversal of the sign of the suspension effect without a corresponding change in sign of the electrophoretic mobility of the suspended particles. The effect seems to be connected with the presence of bi- or polyvalent counterions. An explanation based on the classical theory seems very difficult. In eq. (52), however, in which as we have seen the counterions usually play a predominant part, the transference number of the counterions needs only to become sufficiently negative to explain a reversed suspension effect or Donnan potential. Negative transference numbers in colloidal systems are not abnormal. Cf. data by HARTLEY, COLLIE and SAMIS⁽⁴⁹⁾ on cetyl pyridinium bromide.

6.4. *On the limited use of determining Donnan e.m.f., suspension effect or pH of a suspension*

We have seen that the Donnan e.m.f. and the suspension effect are determined by a rather complicated mixture of mobilities and activities of all the ionic species in the system. Simple relations only exist when the whole system behaves ideally or somewhat less stringently when the electrical potential near the non-diffusible particles remains low ($\psi \ll RT/F$). Only in this case can the Donnan potential be interpreted in a simple way, giving information about the valency of the non-diffusible particles (cf. eq. 15). If the condition of low potential is not fulfilled, however, interpretation is difficult even in the limit of vanishing concentration of colloid. In these circumstances more information can be derived from separate determinations of activities or mobilities.

If this point of view is accepted, one should also realize that the same kind of difficulty may be encountered in the interpretation of the pH of a suspension or polyelectrolyte solution. Much of the value of a pH measurement derives from the assumption that pH gives a reasonable estimate of the activity of the hydrogen ions. This can never be exact because one deals here with a single ion activity but as long as there are reasons to assume that the liquid junction potential with saturated KCl is zero or at least independent of the hydrogen ion activity, the calculation of a_H from pH makes some sense. With polyelectrolytes present in relatively large amounts any such assumption on the *l.j.* potential becomes of doubtful value and an interpretation of the pH in terms of activities of the H^+ ions loses its sense.

It may be good to quote here words used by P. B. TAYLOR⁽⁵⁰⁾ in 1927

in a treatise on pH measurement: “. . . for the cell e.m.f. depends not only on the acid activity but also on the activity of every molecular species in the cell and mobility of every ion. If these are sufficiently well known to be allowed for, the acid activity is likely to be sufficiently well known not to need measurement.”

7. SOME REMARKS ON BIOLOGICAL APPLICATIONS

This paper was aimed at a treatment of some difficulties in non-ideal Donnan equilibria rather than at giving specific applications to biological systems. Three remarks may, however, well be made.

(a) *Qualitatively* there is little difference between the classical approach and that presented here. The suspension has the higher osmotic pressure, the counterions are accumulated in it and quite often to a higher degree than the co-ions are driven away. The sign of the Donnan e.m.f. is the same as the sign of the charge of the particles. Only from the last rule exceptions may be found and explained as suggested in section 6.3. Only if results are to be interpreted *quantitatively*, should a critical attitude prevail. Perhaps unexpectedly the largest deviations from classical Donnan theory may be expected with the most dilute equilibrium solutions.

(b) Donnan systems are (or should be) in equilibrium. In many biological systems membranes separate phases, that are *not* in equilibrium, so that Donnan theory does not apply.

(c) When electrical potentials are measured in biological systems, quite frequently liquid junctions are used to make contact with different parts of the system, e.g. the inside and outside of a nerve fibre. For obvious reasons saturated potassium chloride cannot be used in the liquid junction. A more dilute solution containing far less K-ion is used, e.g. a suitable Ringer solution. The treatment as given in section 6 can be applied to such systems with hardly any modification. It should be realized that the remarkable effect produced by the saturated KCl bridges in the Donnan cell are nearly completely determined by the low concentration side of the liquid junctions and consequently will also be present in these potentials measured in biological systems.

REFERENCES

- (1) DONNAN, F. G. and HARRIS, A. B.; *J. Chem. Soc.* 99 (1911) 1554
DONNAN, F. G.; *Z. Elektrochem.* 17 (1911) 572; *Chem. Revs.* 1 (1924) 73
- (2) GUGGENHEIM, E. A.; *J. Phys. Chem.* 33 (1929) 842
- (3) DONNAN, F. G. and ALLMAND, A. J.; *J. Chem. Soc.* 105 (1914) 1941
- (4) LOEB, J.; *Proteins and the Theory of Colloidal Behaviour*, McGraw-Hill, 2nd ed., p. 178 ff (1924)
- (5) LOEB, J.; *J. Gen. Physiol.* 3 (1921) 85, 547, 667, 691
- (6) WIEGNER, G.; *Kolloid-Z.* 51 (1930) 49
- (7) WIEGNER, G. and PALLMANN, H.; *Z. Pflanzenernähr. Düng. u. Bodenk.* A 16 (1930) 1

REFERENCES

- (8) PALLMANN, H.; *Kolloidchem. Beihefte* 30 (1930) 334
- (9) JENNY, H., NIELSEN, T. R., COLEMAN, N. T. and WILLIAMS, D. E.; *Science* 112 (1950) 164
- (10) COLEMAN, N. T., WILLIAMS, D. E., NIELSEN, T. R. and JENNY, H.; *Soil Sci. Soc. Amer. Proc.* 15 (1951) 106, 111, 114
- (11) MARSHALL, C. E.; *Science* 113 (1951) 43; 115 (1952) 361; *Soil Sci. Soc. Amer. Proc.* 15 (1950) 110; 17 (1953) 218, 221
- (12) PEECH, M. and McDEVIT, W. F.; *Soil Sci. Soc. Amer. Proc.* 15 (1950) 112
- (13) PEECH, M. and SCOTT, A. D.; *ibid.* 15 (1950) 115
- (14) PEECH, M., OLSEN, R. A. and BOLT, G. H.; *ibid.* 17 (1953) 214, 220
- (15) ERIKSSON, E.; *Science* 113 (1951) 418
- (16) MYSELS, K. J.; *Science* 114 (1951) 424; 118 (1953) 603
- (17) BARCOCK, K. L. and OVERSTREET, R.; *Science* 117 (1953) 686
- (18) SOLLNER, K.; *J. Colloid Sci.* 8 (1953) 179
- (19) OVERBEEK, J. TH. G.; *J. Colloid Sci.* 8 (1953) 593
- (20) LOW, P. F.; *Soil Science* 77 (1954) 29
- (21) DONNAN, F. G. and GUGGENHEIM, E. A.; *Z. Physik. Chem.* A 162 (1932) 346
- (22) KAMBYAMA, N.; *Phil. Mag.* (6), 50 (1925) 849
- (23) HÜCKEL, E.; *Kolloid-Z.* 36 (Zsigmondy Festschrift) (1925) 204
- (24) HILL, T. L.; *J. Chem. Phys.* 22 (1954) 7, 1251; cf. also HILL, T. L. in CLARKE, H. T. (Ed.) *Iontransport Across Membranes*. Academic Press, New York, 1954, p. 210 ff
- (25) DAVIS, L. E.; *Soil Science* 54 (1942) 199; 59 (1945) 379
- (26) KLAARENBECK, F. W.; *Over Donnan evenwichten bij solen van Arabische Gom*, Thesis, Utrecht, 1946
- (27) OVERBEEK, J. TH. G.; in KRUYT, H. R. (Ed.) *Colloid Science*, Vol. I, Elsevier, Amsterdam, 1952, pp. 191-193
- (28) GRAHAME, D. C.; *Chem. Revs.* 41 (1947) 441
- (29) DERJAGUIN, B. and LANDAU, L.; *Acta Physicochim. USSR* 14 (1941) 633; *J. Expt. Theor. Physics* (Russ.) 11 (1941) 802; 15 (1945) 662
- (30) VERWEY, E. J. W. and OVERBEEK, J. TH. G.; *Theory of the Stability of Lyophobic Colloids*, Elsevier, Amsterdam, 1948
- (31) HAMMARSTEN, E. and H.; *Arkiv. Kemi. Min. Geol.* 8 (1923) 1
HAMMARSTEN, H.; *Biochem. Z.* 147 (1924) 481
HAMMARSTEN, E.; *Biochem. Z.* 144 (1924) 383
- (32) RIJSSELBERGHE, P. VAN; *J. Phys. Chem.* 38 (1934) 645
- (33) GOUY, G.; *J. Physique* (4) 9 (1910) 457; *Ann. Phys.* (9) 7 (1917) 129
- (34) CHAPMAN, D. L.; *Phil. Mag.* (6) 25 (1913) 475
- (35) JAHNKE, E. and EMDE, F.; *Tables of Functions with Formulae and Curves*, 4th ed., Dover Publications, New York, 1945, p. 52 ff
- (36) BUNGENBERG DE JONG, H. G. and THEUNISSEN, P. H.; *Kolloid. Beih.* 47 (1938) 245
- (37) BRUINS, H. R.; *Kolloid.-Z.* 57 (1931) 152
- (38) OVERBEEK, J. TH. G.; *Bull. Soc. Chim. Belges* 57 (1948) 252
- (39) GUGGENHEIM, E. A.; *J. Phys. Chem.* 33 (1929) 842
- (40) GUGGENHEIM, E. A.; *Thermodynamics*, North Holland Publ. Co., Amsterdam, 1950, p. 332
- (41) MACINNES, D. A.; *The Principles of Electrochemistry*, Reinhold, New York, 1939, p. 221 ff
- (42) OVERBEEK, J. TH. G.; in KRUYT, H. R. (Ed.), *Colloid Science*, Vol. I, Elsevier Amsterdam, 1952, p. 238 ff
- (43) ADAIR, G. S. and ADAIR, M. E.; *Biochem. J.* 28 (1934) 199, 1230
- (44) ADAIR, G. S. and ADAIR, M. E.; *Trans. Faraday Soc.* 31 (1935) 130

THE DONNAN EQUILIBRIUM

- (45) ADAIR, G. S. and ADAIR, M. E.; *Trans. Faraday Soc.* 36 (1940) 23
(46) CHARLWOOD, P. A.; *Biochem. J.* 46 (1950) 312
(47) TISELIUS, A. and SVENSSON, H.; *Trans. Faraday Soc.* 36 (1940) 16
(48) RAUPACH, M.; *Austral. J. Agric. Res.* 5 (1954) 716
(49) HARTLEY, G. S., COLLIE, B. and SAMIS, C. S.; *Trans. Faraday Soc.* 32 (1936)
795
(50) TAYLOR, P. B.; *J. Phys. Chem.* 31 (1927) 1499