

# Regulation of Surface Potential at Amphoteric Surfaces during Particle-Particle Interaction

BY D. CHAN, J. W. PERRAM AND L. R. WHITE

Department of Applied Mathematics, Institute of Advanced Studies,  
Australian National University, Canberra ACT, Australia

AND

T. W. HEALY\*

Department of Physical Chemistry, University of Melbourne,  
Parkville 3052, Victoria, Australia

*Received 19th February, 1974*

A model is presented whereby a system of two interacting electrical double layers can minimise its electrical free energy at all distances of separation. The surface charge on each particle is described in terms of surface site equilibria which maintain constant chemical potential of potential determining ions. The ability of the system to react (i.e. buffer) to changes in the interparticle medium during approach, depends on the surface site dissociation constants, the point of zero charge of the surface and the ionic strength. It is shown that essentially perfect regulation, i.e. essentially infinite buffer capacity, is observed with systems such as AgI for which the potential of the single double layer is given by the Nernst equation; for such a system the usual assumption of interaction at constant potential is sensibly correct. For systems where the activity of potential determining ions is set at a value far removed from a surface dissociation constant the interaction is well approximated by constant charge interaction. The interaction with regulation involves solving a set of transcendental equations for self consistent values of surface charge and potential at all separations for any given set of bulk parameters. It is a general treatment that replaces constant charge and constant potential assumptions and is applicable to oxide colloids and amphoteric biosurfaces in particular.

---

## INTRODUCTION

In using the formalism of the Deryaguin-Landau-Verwey-Overbeek theory to calculate the stability of lyophobic colloids it has been necessary to assume that constant charge or constant potential is maintained on either or both surfaces during collision.<sup>1</sup> Certain surfaces where the charge is due, for example, to strong acid sites may indeed need to be considered in terms of interactions at constant charge. There is as yet no criterion for selecting the extent to which such an assumption is valid, nor is there a criterion for determining *a priori* whether constant charge or constant potential interaction may be more appropriate for many other important colloidal systems.

There has been a somewhat uncritical acceptance of the assertion that constant surface charge interaction is more appropriate to coagulation of AgI or hydrous oxide colloids. While Frens and Overbeek<sup>2-4</sup> did show that perturbation of bulk electrolyte composition resulted in relatively slow restitution of the equilibrium potential of a Ag/AgI electrode, there is as yet no direct measurement of the ability or otherwise of particles to adjust ion populations at the surface and in the interparticle fluid during collision.

The reason that one is forced to choose between constant charge and constant

potential is that until recently there has been no explicit relationship available for the charge and potential in an interacting system. The present paper represents an extension of the method of Ninham and Parsegian<sup>5</sup> (N.P.) in which the electrostatic potential between two surfaces is regulated during approach by those equilibria at the surface that are responsible for the development of the surface charge itself.

The solid/liquid interface is considered to develop a surface charge as a result of surface equilibria involving potential determining ions (p.d.i.) which give rise to positive, negative, and for some systems, neutral surface sites. It is considered that the approach of the two identical † surfaces is sufficiently slow that electrochemical equilibrium is maintained at all times during collision. This is not an assumption of "constant potential"; indeed it will be shown that if conditions are such that regulation of the surface potential and charge is limited, then *both* charge and potential will change significantly during the interaction *or* if conditions are favourable for regulation then changes in charge *and* potential will be minimal during interaction.

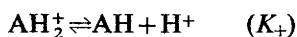
The N.P. model as extended herein to a general amphoteric surface involves surface equilibria that are controlled by the chemical potential of p.d.i. in bulk solution.

It is a general treatment and it is not necessary to specify the nature of the p.d.i. However for the purposes of comparing the theoretical result with experiment, it is convenient to specify that  $H^+$  and  $OH^-$  are p.d.i., as, for example,  $Fe_2O_3$  etc. or organic colloids with amine, carboxylate, sulphonate etc. surface groups.

#### GENERAL FORMALISM

We consider the regulation of the electrostatic potential between surfaces bearing ionizable groups and we generalize the N.P. model to include amphoteric surfaces, i.e. ones where equilibria can generate nett positive or nett negative sites depending on the activity of p.d.i. in the bulk solution. In the interest of mathematical simplicity we will not include the effect of divalent ions. In view of the existence of the N.P. treatment we will omit here most of the mathematical steps and concentrate on the method used. For more detailed treatment and the inclusion of divalent ions, the reader is referred to the original paper.<sup>5</sup>

We consider initially a planar halfspace of the amphoteric substance in contact with a solution of 1 : 1 electrolyte whose bulk pH may be controlled. The reactions at the surface are,



where  $AH_2^+$ ,  $AH$  and  $A^-$  represent positive, neutral and negative surface sites respectively, the relative concentrations of which are determined by the hydrogen ion concentration at the surface,  $H_s$ , i.e.

$$[AH]H_s = [AH_2^+]K_+ \quad (1)$$

$$[A^-]H_s = [AH]K_- \quad (2)$$

where  $K_+$  and  $K_-$  are the effective acid ionization constants for the above equilibria. The validity of eqn (1) and (2) is examined below.

The chemical potential of a species  $i$  can always be written as

$$\mu_i = \mu_i^\circ + kT \ln C_i + kT \ln \gamma_i$$

where the last term represents the concentration dependent part of the free energy of

† The case of interaction of dissimilar double layers under conditions of regulation has been considered and will be published at a later date.<sup>6</sup>

interaction of species  $i$  with its environment. Any concentration independent terms are grouped in the constant  $\mu_i^\circ$ . This equation may be taken as a definition of the activity coefficient  $\gamma_i$ .

Consider the species  $\text{AH}$ ,  $\text{AH}_2^+$ ,  $\text{A}^-$  involved in the surface reaction given by eqn (1) and (2). The interaction of a molecule of the charged species can be divided into two parts: an electrostatic interaction with the local potential caused by all the charges on the surface and in the electrolyte, and a dispersion interaction with its neighbouring molecules. The uncharged species will only have the dispersion contribution. The local electrostatic potential can, with no loss of generality, be considered, as by Levine and Smith,<sup>10</sup> to be the sum of the macroscopic potential (determined by the Poisson-Boltzmann equation) and a fluctuating term which accounts for the local deviations from the average behaviour. We write

$$\mu_{\text{AH}_2^+} = \mu_{\text{AH}_2^+}^\circ + kT \ln [\text{AH}_2^+] + e\psi_0 + kT \ln \gamma_+$$

$$\mu_{\text{A}^-} = \mu_{\text{A}^-}^\circ + kT \ln [\text{A}^-] - e\psi_0 + kT \ln \gamma_-$$

$$\mu_{\text{AH}} = \mu_{\text{AH}}^\circ + kT \ln [\text{AH}] + kT \ln \gamma_0$$

where the terms involving  $\gamma_+$ ,  $\gamma_-$ ,  $\gamma_0$  represent the dispersion interaction energy and the fluctuating "local" part of the electrostatic energy. Equilibrium requires

$$\mu_{\text{AH}} + \mu_{\text{H}^+} = \mu_{\text{AH}_2^+}$$

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

where

$$\mu_{\text{H}^+} = \mu_{\text{H}^+}^\circ + kT \ln [\text{H}^+]_s + kT \ln \gamma_{\text{H}^+}$$

is the chemical potential of the p.d.i. These equations may be arranged to give

$$\frac{[\text{AH}][\text{H}^+]_s}{[\text{AH}_2^+]} = \frac{\gamma^+}{\gamma_0 \gamma_{\text{H}^+}} K_+^\circ$$

$$\frac{[\text{A}^-][\text{H}^+]_s}{[\text{AH}]} = \frac{\gamma_0}{\gamma_- \gamma_{\text{H}^+}} K_-^\circ$$

where the constants  $K_+^\circ$  and  $K_-^\circ$  are

$$K_+^\circ = \exp[-(\mu_{\text{AH}}^\circ + \mu_{\text{H}^+}^\circ - \mu_{\text{AH}_2^+}^\circ)/kT]$$

$$K_-^\circ = \exp[-(\mu_{\text{A}^-}^\circ + \mu_{\text{H}^+}^\circ - \mu_{\text{AH}}^\circ)/kT].$$

In general the ratios of activity coefficients are not independent of  $[\text{A}^-]$ ,  $[\text{AH}_2^+]$ ,  $[\text{AH}]$  and  $[\text{H}^+]_s$ . To calculate the functional dependence of these ratios on the relevant concentrations, we would need a statistical theory of surface activity coefficients for high concentrations, and such a theory is not available.

Two points should be made. First, we are interested in elucidating qualitatively the physics of interaction of amphoteric surfaces. To do this in the absence of a theory of surface activity coefficients, all that is required is that the ratios of activity coefficients remain sensibly constant as the surfaces approach each other so that the ratios of concentrations of species involved in a reaction can be given by an effective dissociation constant. Since the ratio of activity coefficients is of the order unity, and  $pK^\circ \approx 3-8$  then  $pK \approx pK^\circ$  for each reaction.

Secondly, sound physical arguments can be invoked to show that  $\gamma_+ \approx \gamma_- \approx \gamma_0$ . The layers of surface sites may be considered to be sandwiched between a dielectric half space and the electrolyte half space. Calculations of the electrostatic interaction between charged species in the surface layer show that such interactions are very

strongly screened by image forces in the dielectric and the electrolyte. Thus the contribution from the local electrostatic potential (with the macroscopic potential  $\psi_0$  subtracted out) to the interaction energy of a charged species is very much reduced from that of a coulomb type interaction. The dispersion energy contribution will then be a large part of the total interaction energy. Further, since all the species  $\text{AH}_2^+$ ,  $\text{AH}$ ,  $\text{A}^-$  are basically the same molecular unit, their polarizabilities and therefore their dispersion interaction energies with species on neighbouring sites will be largely independent of their charge.

These arguments imply that the interaction energies of the surface species are to a large degree independent of the species and are approximately functions of the density of surface sites only. Therefore, the activity coefficients will be approximately equal. The activity coefficient of the p.d.i. near the surface is, of course, a function of the surface concentration  $H_s$  of the p.d.i., which in turn is determined by the surface potential. As we shall show later,  $\psi_0$  is roughly constant in an equilibrium approach and thus  $H_s$  does not change too dramatically during such an approach. Since activity coefficients are moderately insensitive functions of concentration, the surface activity coefficient of the p.d.i. at infinite separation should be a good approximation to the surface activity coefficient during approach.

Such arguments justify, then, the use of effective dissociation constants

$$K_+ = \frac{\gamma_+}{\gamma_0 \gamma_{\text{H}^+}} K_+^0$$

$$K_- = \frac{\gamma_0}{\gamma_- \gamma_{\text{H}^+}} K_-^0$$

to describe the surface equilibrium during approach. It should be noted that experiments on stable colloid systems<sup>11</sup> yield this effective dissociation constant.

If there are  $N_s$  sites per unit area of surface at which the reactions may occur then the charge density on the surface  $\sigma_0$  is given by

$$\sigma_0 = N_s e (\theta_+ - \theta_-) \quad (3)$$

where

$$\theta_+ = \frac{[\text{AH}_2^+]}{[\text{AH}] + [\text{AH}_2^+] + [\text{A}^-]} = \frac{[\text{AH}_2^+]}{N_s} \quad (4)$$

$$\theta_- = \frac{[\text{A}^-]}{[\text{AH}] + [\text{AH}_2^+] + [\text{A}^-]} = \frac{[\text{A}^-]}{N_s} \quad (5)$$

are the fractions of the total surface density of sites ionized positively and negatively. The quantity  $\sigma_0$  is the experimental (titratable) surface charge for simple systems that do not involve site binding by indifferent ions. The more complex system has been considered elsewhere.<sup>7</sup>

From eqn (1), (2) and (3),

$$\frac{\sigma_0}{N_s e} = \frac{(H_s/K_+ - C/H_s)}{1 + H_s/K_+ + K_-/H_s} \quad (6)$$

The surface charge gives rise to an electrical double layer which modifies the ion concentrations in the solution. If  $H$  and  $C$  are the bulk concentrations of hydrogen ion and inert positive ions in solution, then

$$[\text{H}] = H \exp(-e\psi/kT) \quad (7)$$

$$[\text{C}] = C \exp(-e\psi/kT) \quad (8)$$

are the concentration in solution where the electrostatic potential is  $\psi$ . For a surface potential  $\psi_0$  we have

$$H_s = H \exp(-e\psi_0/kT) \quad (9)$$

so that the surface charge may be written

$$\sigma_0 = N_s e \frac{(H/K_+) \exp(-e\psi_0/kT) - (K_-/H) \exp(+e\psi_0/kT)}{1 + (H/K_+) \exp(-e\psi_0/kT) + (K_-/H) \exp(+e\psi_0/kT)}. \quad (10)$$

If we define the total concentrations of positive and negative species as

$$c_+ = [H^+] + [C] \quad (11)$$

$$c_- = [OH^-] + [\text{negative inert species}] \quad (12)$$

then

$$c_+ = c \exp(-e\psi/kT) \quad (13)$$

$$c_- = c \exp(+e\psi/kT) \quad (14)$$

where

$$c = H + C. \quad (15)$$

The charge density at a point in the solution where the potential is  $\psi$  is given by

$$\begin{aligned} \rho &= \frac{N_0 e}{10^3} (c_+ - c_-) \\ &= \frac{N_0 e c}{10^3} [\exp(-e\psi/kT) - \exp(+e\psi/kT)]. \end{aligned} \quad (16)$$

All concentrations are measured in units of mol cm<sup>-3</sup> and  $N_0$  is Avogadro's Constant.

The potential and charge density are related through the equation

$$\nabla^2 \psi = -4\pi\rho/\epsilon. \quad (17)$$

For an isolated surface <sup>1</sup>

$$\sigma = \frac{\epsilon \kappa k T}{2\pi e} \sinh(e\psi_0/2kT) \quad (18)$$

where

$$\kappa^2 = 8\pi N_0 c e^2 / 10^3 \epsilon k T. \quad (19)$$

For given bulk concentration,  $H$  and  $C$ , eqn (10) and (18) constitute a transcendental equation for  $\psi_0$ . Thus  $\psi_0$  can be varied by adjustment of the bulk pH and inert electrolyte concentration.

In what follows we shall ignore the possibility of Stern layer formation at the surface. The mechanism of regulation will not be drastically altered by the inclusion of the Stern layer and since we are interested, here, in the important aspect of regulation only, it is not necessary at this stage to model the surface region with a more sophisticated theory.

We wish to examine the surface potential as a function of separation as we bring two of these surfaces together from infinity. We set up an axis system with the  $z$  axis perpendicular to the surfaces and the origin at the left-hand surface. The surfaces are at  $z = 0, 2L$ . From the symmetry of the problem we need solve eqn (17) only in the region  $0 \leq z \leq L$ , subject to the boundary conditions

$$\left. \frac{d\psi}{dz} \right|_{z=L} = 0 \quad (20)$$

$$\left. \frac{d\psi}{dz} \right|_{z=0} = \frac{-4\pi\sigma_0}{\epsilon}. \quad (21)$$

Using eqn (16) Poisson's equation (17) in this axis system becomes

$$\frac{d^2\psi}{dz^2} = \frac{4\pi N_0 c e}{10^3 \epsilon} [\exp(e\psi/kT) - \exp(-e\psi/kT)]. \quad (22)$$

The substitutions

$$\phi = \exp(-e|\psi|/2kT) \quad (23)$$

$$\phi_L = \exp(-e|\psi_L|/2kT) \quad (24)$$

(where  $\psi_L$  is the midplane potential) and the boundary conditions (20) enable us to solve eqn (22) in the N.P. form

$$\phi = \phi_L cd\left(\frac{\kappa(L-z)}{2\phi_L}; \phi_L^2\right) \quad (25)$$

where  $cd(x; k)$  is a Jacobi elliptic function<sup>8</sup> with argument  $x$  and modulus  $k$ .

Using the fact that

$$\frac{d}{dx} cd(x; k) = (k^2 - 1) \frac{\text{sn}(x; k)}{\text{dn}^2(x; k)} \quad (26)$$

(where  $\text{sn}$  and  $\text{dn}$  are Jacobi elliptic functions) the boundary condition (21) may be written

$$|\sigma_0| = \left(\frac{kT}{\pi\kappa e}\right) \frac{\phi_L(\phi_L^4 - 1) \text{sn}\left(\frac{\kappa L}{2\phi_L}; \phi_L^2\right)}{cd\left(\frac{\kappa L}{2\phi_L}; \phi_L^2\right) \text{dn}^2\left(\frac{\kappa L}{2\phi_L}; \phi_L^2\right)}. \quad (27)$$

From (25)

$$\begin{aligned} \phi_0 &= \exp(-e|\psi_0|/2kT) \\ &= \phi_L cd\left(\frac{\kappa L}{2\phi_L}; \phi_L^2\right). \end{aligned} \quad (28)$$

Eqn (10), (27) and (28) constitute a single transcendental equation to be solved for  $\phi_L$ . Thus  $\psi_0$  and  $\sigma_0$  may be found self consistently as functions of the separation  $2L$ , for given bulk concentrations  $H$  and  $C$ .

From eqn (10) and (27) it can be shown (see Appendix I) that the following asymptotic results are obtained:

i.e. as  $L \rightarrow 0$  (for fixed  $\kappa$ )

$$\sigma_0 \rightarrow 0$$

$$\psi_0 \rightarrow \psi_L \rightarrow 2.303(kT/e)(\text{pH} - \text{pH}_{\text{pzc}})$$

where  $\text{pH}_{\text{pzc}}$  is the bulk pH corresponding to the point of zero charge which will be identical to the pH of the isoelectric point if indifferent electrolyte only is present. The p.z.c. is related to surface equilibrium constants by

$$\text{pH}_{\text{pzc}} = \frac{1}{2}(\text{p}K_+ + \text{p}K_-).$$

That  $\psi_0$  is given by a Nernst equation at zero separation has been noted earlier by Frens and Overbeek.<sup>3</sup>

## RESULTS

In order to examine the effect of regulation on the surface charge and potential it is necessary to select values of  $K_+$  and  $K_-$ , the surface dissociation constants;  $N_s$  is taken as  $5 \times 10^{14}$  site  $\text{cm}^{-2}$  following earlier work. While the preceding is general

for any p.d.i. it has been set up in terms of  $H^+$  and  $OH^-$  as p.d.i. oxides. It is appropriate to consider two classes of oxides <sup>7</sup> for which  $\Delta pK$ , i.e. ( $pK_- - pK_+$ ), is small (e.g.  $TiO_2$ ,  $Fe_2O_3$ ,  $Al_2O_3$ ), and, for which  $pK$  is large (e.g.  $SiO_2$ , sulphonated lattices). Again since it is important for comparison purposes to keep  $\kappa$  constant while changing the pH over a wide range, the following two cases have been selected:

$$(A) \text{ pH}_{pzc} = 7 \quad pK_+ = 5.5, \quad pK_- = 8.5;$$

$$(B) \text{ pH}_{pzc} = 7, \quad pK_+ = 4, \quad pK_- = 10.$$

The variation in  $\psi_0$  with separation for  $10^{-3}$  mol  $dm^{-3}$  electrolyte ( $1/\kappa = 96 \text{ \AA}$ ) for these two cases is shown in fig. 1A and B. The simultaneous variation of  $\sigma_0$  as a function of separation is shown in fig. 2 for several values of the potential of a single double layer and for the two  $\Delta pK$  values of 3 and 6.

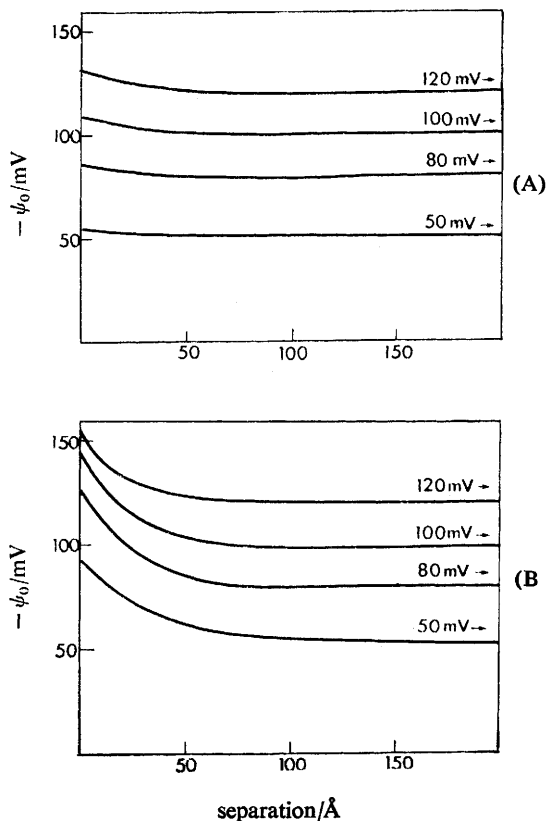


FIG. 1.—Variation of the total double layer potential ( $\psi_0$ ) with distance of separation of two surfaces having points of zero charge at pH 7 for (A)  $\Delta pK = 3$  and (B)  $\Delta pK = 6$ . The potentials shown at the right on each curve are the potentials at infinite separation.

Finally the effect of changing  $\kappa$  on the variation of  $\psi_0$  with separation is shown in fig. 3 for  $10^{-2}$  and  $10^{-4}$  mol  $dm^{-3}$  supporting electrolyte for the case of  $\Delta pK = 3$ .

In order to illustrate the difference between the present regulation mechanism and that appropriate to a constant charge system,  $\psi_0$  as a function of  $L$  has been computed for constant charge conditions. In fig. 4 the dashed lines represent the change in

surface potential for interaction at constant charge (the charge being fixed at the value at infinite separation). The solid lines represent the same system under regulation, imposed by  $pK_+ = 3$  and  $pK_- = 9$  and  $pH_{pzc} = 6$ , at  $10^{-3}$  mol  $dm^{-3}$  ionic strength.

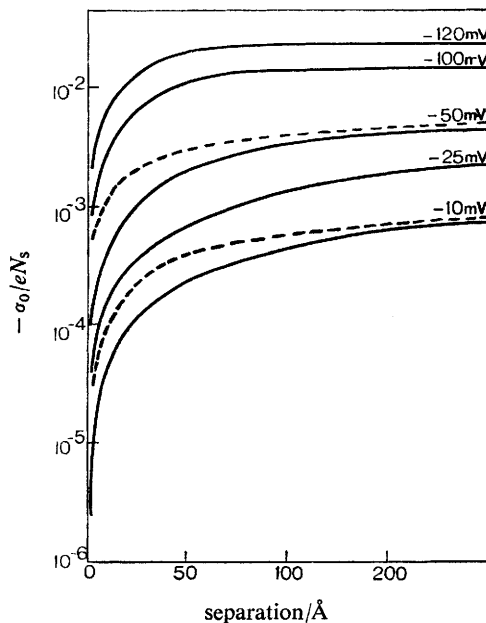


FIG. 2.—Variation of the surface charge ( $\sigma_0$ ) with distance of separation of two surfaces having points of zero charge at pH 7 for  $\Delta pK = 3$  (solid lines) and  $\Delta pK = 6$  (dashed lines). The potentials shown at the right on each curve are the potentials at infinite separation. The ionic strength is  $10^{-3}$  mol  $dm^{-3}$  in each example.

## DISCUSSION

The present model of a system of two interacting double layers differs from earlier models in that surface site dissociation via  $K_+$  and  $K_-$  provides a mechanism whereby chemical potentials can be maintained constant during interaction. The surface regulation model is not a constant surface potential model but one in which the boundary conditions on the gradient and magnitude of the potential are determined self-consistently by the relationship between surface charge and potential given by eqn (10).

Physically, surface regulation is a feedback mechanism involving the following for the case of, say, two positive surfaces; as the double layers come together the potential begins to rise, thereby decreasing the surface concentration of hydrogen ions. Dissociation of  $AH_2^+$  groups occurs to maintain equilibrium so that  $\sigma_0$  the surface charge now decreases which from eqn (10) results in a decrease in surface potential. In general terms, the feedback mechanism is able to work because of the buffer capacity of the surface and regulation will minimise changes in surface potential at the expense of surface charge; the surface charge must be zero at zero separation. The regulation effect is demonstrated quantitatively in fig. 1 and 2, where it can be seen that neither charge nor potential is constant during interaction. Considering the change in potential with separation (fig. 1 and 3) it can be seen that  $\Delta pK$  exerts an important effect on regulation so that as  $\Delta pK$  increases the ability of the surface to



enforce regulation decreases. This is better illustrated by considering the results of fig. 5 where the magnitude of the nett surface charge is plotted against the surface pH i.e.  $-\log [H]_s$  or  $pH_s$ . From eqn (9)

$$pH_s = pH + \frac{e}{2.303RT} \psi_0.$$

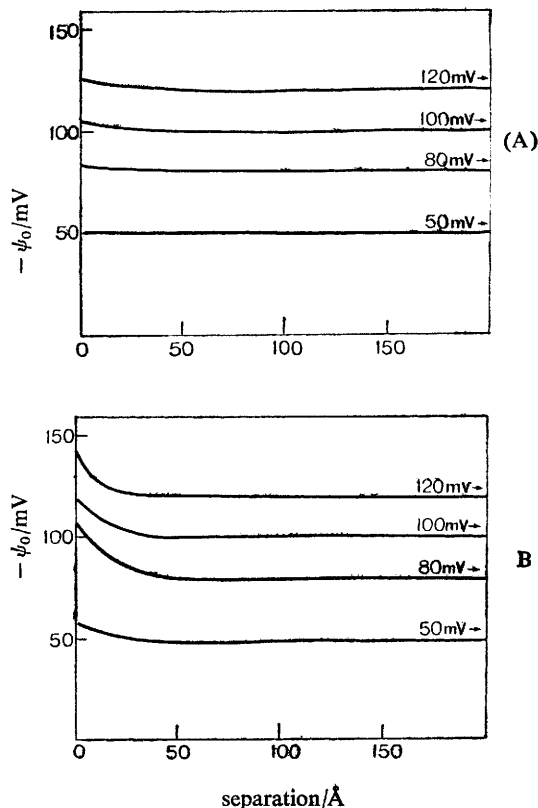


FIG. 3.—Variation of the total double layer potential ( $\psi_0$ ) with distance of separation of two surfaces having points of zero charge of 7 and for (A)  $\Delta pK = 3$ ,  $10^{-4}$  mol  $\text{dm}^{-3}$  ionic strength and (B)  $\Delta pK = 6$ ,  $10^{-2}$  mol  $\text{dm}^{-3}$  ionic strength.

Three cases are shown viz.  $\Delta pK = 6$ , 3 and the limit of zero where  $pK_+ = pK_- = pH_{pzc}$ . The region of  $pH_s$  around the  $pH_{pzc}$ , where  $\sigma_0$  is an insensitive function of  $pH_s$ , increases as  $\Delta pK$  increases. Since regulation depends on the degree to which  $\sigma_0$  can respond to changes in  $\psi_0$ , then as shown in fig. 1A and B the smaller the  $\Delta pK$  the better the regulation. For any  $\Delta pK$  as  $\sigma_0 \rightarrow 0$  (i.e.  $L \rightarrow 0$ )  $\psi_0$  is unable to be regulated. Similarly as  $\psi_0$  at infinite separation goes to zero the *proportional* change in  $\psi_0$  increases. Again for small  $\psi_0$  and/or for  $L \rightarrow 0$  for any  $\psi_0$  the system is in the flat-insensitive region of fig. 5.

At large values of  $|\psi_0|$  where  $pH_s \gg pK_-$  (or  $pH_s \ll pK_+$ ) as seen in fig. 5, the surfaces are almost fully charged and again  $\sigma_0$  is an insensitive function of  $\psi_0$  (or  $pH_s$ ) and regulation will be poor. In this case, the system now approaches constant charge conditions until small values of separation where  $\sigma_0$  must decrease directly to zero.

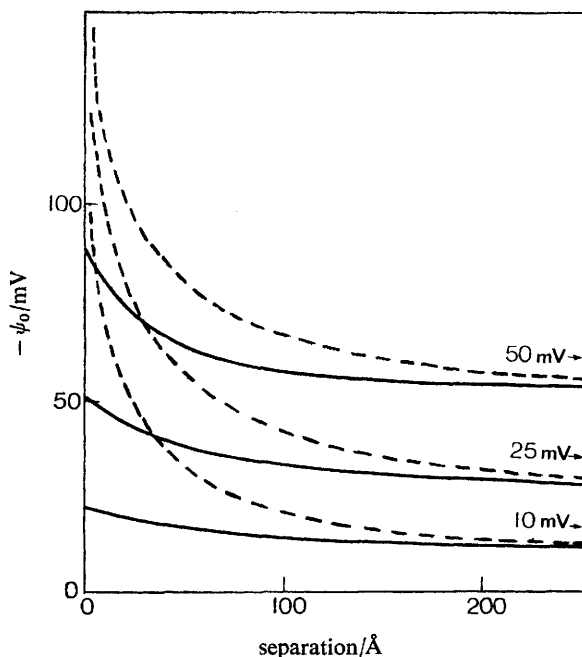


FIG. 4.—Comparison of the change in total double layer potential ( $\psi_0$ ) during interaction under constant charge conditions (dashed lines) and under regulated interaction (solid lines). The  $\Delta pK$ , ionic strength and point of zero chosen are 6,  $10^{-3}$  mol  $\text{dm}^{-3}$  and pH 6 respectively.

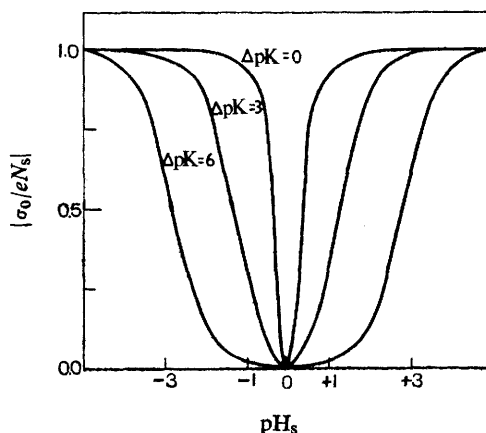


FIG. 5.—Variation of the surface charge ( $\sigma_0$ ) with surface pH [as defined by eqn (9)] for three values of  $\Delta pK$  of 6, 3 and 0. The point of zero charge is taken as pH 7.

An important consequence of regulated interaction is that when the system can regulate,  $\psi_0$  is kept remarkably constant during approach when compared with interaction, as shown in fig. 4, at constant surface charge. Thus, comparing the electrostatic free energy of repulsion for constant charge and the regulated case it can be shown that the system minimises its energy best under regulated approach.\* This

\* Regulation involves maintenance of equilibrium at all distances of approach and is necessarily the lowest energy interaction.

is shown in fig. 6, where the electrostatic free energy of interaction ( $V_R$ ) is plotted as a function of distance of separation for regulated approach, constant potential approach and constant charge approach. The constant potential case is in fact perfect regulation as was stressed by Verwey and Overbeek.<sup>9</sup> This can be established from eqn (1), (2) and (9), since it follows that

$$\psi_0 = (2.30 kT/e)(\text{pH}_{\text{pzc}} - \text{pH}) - (kT/2e) \ln([\text{AH}_2^+/\text{A}^-]). \quad (29)$$

As discussed above, regulation depends on the  $\Delta\text{p}K$  for any given pH. The case of  $\Delta\text{p}K = 0$ , i.e.  $\text{p}K_+ = \text{p}K_- = \text{pH}_{\text{pzc}} = 7$  of fig. 5 is not perfect regulation. For this hypothetical case the fraction of neutral (AH) surface sites is  $\frac{1}{3}$ , i.e. finite and as discussed by Levine and Smith<sup>10</sup> the  $\ln$  term of eqn (29) approaches zero as the fraction of neutral sites approaches zero.

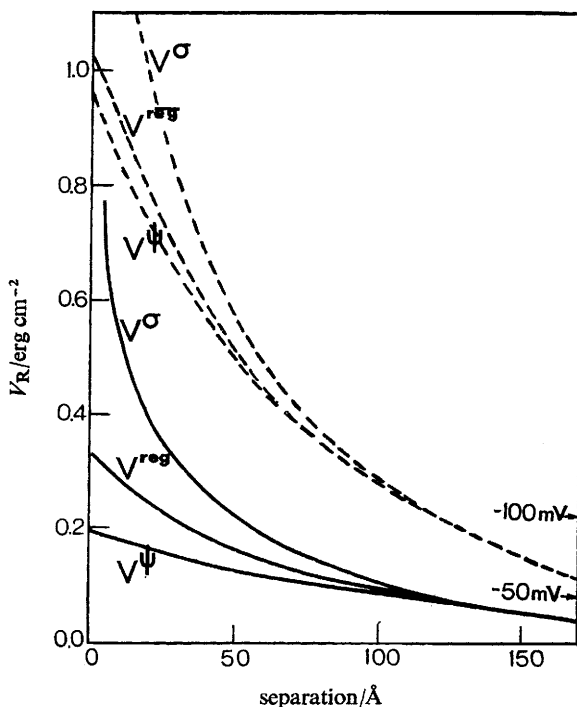


FIG. 6.—Comparison of the electrostatic free energy of interaction ( $V_R$ ) as a fraction of separation for interaction at constant charge ( $V_R^\sigma$ ), constant potential ( $V_R^\psi$ ) and under regulation ( $V_R^{\text{reg}}$ ) imposed by  $\Delta\text{p}K$  3 (dashed lines) and  $\Delta\text{p}K$  6 (solid lines) at points of zero charge of 7. In all cases, the ionic strength is  $10^{-3}$  mol  $\text{dm}^{-3}$ . The potentials shown at the right of each set of curves are the potentials at infinite separation.

However, even in the case where there are no neutral sites, e.g. the  $\text{AgI}/\text{H}_2\text{O}$  interface, if  $\psi_0$  is finite the  $\ln$  term cannot be zero. For this case of charged sites only the  $\ln$  term will be close to zero and at all distances the surface potential will be essentially the Nernst potential. Since we have shown that for any system the asymptotic value of the surface potential at  $L = 0$  is the Nernst potential then a system of no neutral sites is a very close approximation to constant potential. In other words, any system that obeys the Nernst equation at infinite separation will conform closely to a constant potential interaction.

The regulated approach analysis of double layer penetration has two important limits, viz. for systems where the Nernst equation is sensibly obeyed at infinite separation then approach is sensibly at constant potential. In addition if  $\psi_0$  is such that the  $\psi_0$ - $\sigma_0$  relationship is essentially insensitive to changes in  $\psi_0$ , the approach is essentially constant charge interaction until very small distances.

The fundamental assumption in the classical D.L.V.O. constant potential interaction or the present N.P. regulated interaction is that equilibrium is maintained at all separations. This is obeyed if the two interacting surfaces come together at a rate that is less than the rate of attainment of equilibrium. If the system cannot regulate during the time of collision a constant charge interaction is appropriate. If particles cross a coagulation barrier that is due to a constant charge interaction, the surfaces of particles in the aggregate will then have time to regulate their surface potentials and peptization under regulation will occur.

If the potential energy barrier under constant charge conditions is of the order of or just greater than the average kinetic energy of the particles then the velocity of approach may become slow enough that a change during collision from constant charge to regulated interaction is possible. The potential energy barrier under regulated interaction is lower than that under constant charge approach and instability which would not be predicted under constant charge approach may be observed.

#### APPENDIX

We wish to determine from eqn (27) the behaviour of the surface charge and the surface potential in the limit of small separation ( $L \rightarrow 0$ ). Using the series expansions for the elliptic functions,<sup>8</sup> we see that, to leading order in the argument :

$$\operatorname{sn}(u; k) = u + \mathcal{O}(u^3)$$

$$\operatorname{cd}(u; k) = 1 + \mathcal{O}(u^2)$$

$$\operatorname{dn}(u; k) = 1 + \mathcal{O}(u^2).$$

Therefore the right hand side of eqn (27) tends to zero as  $L \rightarrow 0$  that is, the surface charge  $\sigma_0$  tends to zero. Hence from eqn (10)

$$\Psi_0 = 2.303 kT/e (\text{pH}_{\text{pzc}} - \text{pH}).$$

For a detailed asymptotic analysis of the small separation regime the reader is referred to the original paper.<sup>5</sup>

One of us (T. W. H.) thanks the Australian Research Grants Commission for support of part of this work.

<sup>1</sup> E. J. Verwey and J. Th. G. Overbeek, *Theory of the Stability of Lyophobic Colloids* (Elsevier, Amsterdam, 1948).

<sup>2</sup> G. Frens, D. J. C. Engel and J. Th. G. Overbeek, *Trans. Faraday Soc.*, 1967, **63**, 418.

<sup>3</sup> G. Frens and J. Th. G. Overbeek, *J. Colloid Interface Sci.*, 1972, **38**, 376.

<sup>4</sup> G. Frens, *Thesis* (Utrecht, 1968).

<sup>5</sup> B. W. Ninham and V. A. Parsegian, *J. Theor. Biol.*, 1971, **31**, 405.

<sup>6</sup> D. Chan, T. W. Healy and L. R. White, in preparation.

<sup>7</sup> D. E. Yates, S. Levine and T. W. Healy, *Trans. Faraday Soc. I*, 1974, **70**, 1807.

<sup>8</sup> E. T. Whittaker and G. N. Watson, *A Course of Modern Analysis* (Cambridge University Press, 1969).

<sup>9</sup> ref. (1), p. 61.

<sup>10</sup> S. Levine and A. L. Smith, *Disc. Faraday Soc.*, 1971, **52**, 290.

<sup>11</sup> P. W. Schindler and H. Gamsjager, *Disc. Faraday Soc.*, 1971, **52**, 286.