THE SOLID / LIQUID INTERFACE

G. A. BOOTSMA, N. F. DE ROOIJ and A. VAN SILFHOUT

*Twente University of Technology, Department of Applied Physics, 7500 AE Enschede
 (The Netherlands)*

Contents	page
1 Gibbs adsorption equation	111
1.1 Thermodynamics	111
1.2 Gibbs' interfacial model	114
2 Electrical aspects	116
2.1 Types of potentials	116
2.2 Gibbs adsorption isotherm at charged interfaces	118
2.3 Nernst equation, potential determining ions	120
2.4 Gouy–Chapman–Stern model of the electrical double layer	122
3 Applications	124
3.1 Galvanic cell	124
3.2 Oxide/electrolyte interface	125
3.3 Interface between semiconductor and oxide layer	128
3.4 ISFET	132
References	135

1 Gibbs adsorption equation [1–4]

1.1 Thermodynamics

In the macroscopic description of an interface, $i.e.$, the transition region (σ) between two homogeneous parts of a system (the phases α and β), the thermodynamic quantity γ is the central parameter. For a system with components i the reversible changes in the internal energy U and Gibbs free energy G are given by

$$dU = TdS - pdV + \sum_i \mu_i dn_i + \gamma dA, \quad (1)$$

and

$$dG = -SdT + Vdp + \sum_i \mu_i dn_i + \gamma dA \quad (2)$$

Here p (pressure), T (temperature), μ_i (thermodynamic potential of component i) and γ (interfacial or surface tension) are intensive properties, and U , G , S (entropy), V (volume), n_i (number of moles of component i) and A

(interfacial area) are extensive properties of the system. According to eqn (2) γ is defined as the Gibbs free energy of formation of the interface, *i.e.*, the reversible work required to create a unit of interface in the usual experimental conditions

$$\gamma = \left(\frac{\partial G}{\partial A} \right)_{p, T, n_i} \quad (3)$$

Based on eqn (1), γ can be related to the interfacial energy as

$$\gamma = \left(\frac{\partial U}{\partial A} \right)_{p, T, n_i} + T \left(\frac{\partial \gamma}{\partial T} \right)_{p, A, n_i} + p \left(\frac{\partial \gamma}{\partial p} \right)_{T, A, n_i}, \quad (4)$$

where use has been made of Maxwell's relations derived from eqn (2). In thermodynamic equilibrium the intensive parameters T and the μ_i 's are constant throughout the system, as well as p if the interface between α and β is flat. For the individual phases, the expressions corresponding with eqn (1) may then be written as

$$dU^\alpha = TdS^\alpha - pdV^\alpha + \sum_i \mu_i dn_i^\alpha, \quad (5a)$$

$$dU^\beta = TdS^\beta - pdV^\beta + \sum_i \mu_i dn_i^\beta \quad (5b)$$

These expressions may be integrated and subsequently differentiated to yield, after subtraction of eqns 5(a), (b) the Gibbs–Duhem relations

$$-S^\alpha dT + V^\alpha dp - \sum_i n_i^\alpha d\mu_i = 0, \quad (6a)$$

$$-S^\beta dT + V^\beta dp - \sum_i n_i^\beta d\mu_i = 0 \quad (6b)$$

If we denote the extensive properties of the interface with the superscript σ , the following relations will hold for the total system

$$n_i = n_i^\alpha + n_i^\beta + n_i^\sigma, \quad (7)$$

$$U = U^\alpha + U^\beta + U^\sigma, \quad (8)$$

$$S = S^\alpha + S^\beta + S^\sigma, \quad (9)$$

$$V = V^\alpha + V^\beta + V^\sigma \quad (10)$$

Subtraction of eqns (5a) and (5b) from eqn (1) yields, with eqns (7)–(10)

$$dU^\sigma = TdS^\sigma + \sum_i \mu_i dn_i^\sigma + \gamma dA - pdV^\sigma \quad (11)$$

This equation may again be integrated and subsequently differentiated to give, after subtraction of eqn (11), the interface analogue of the Gibbs–Duhem relation

$$-V^\sigma dp + S^\sigma dT + \sum_i n_i^\sigma d\mu_i + A d\gamma = 0 \quad (12)$$

After introducing the definitions

$$\tau = \frac{V^\sigma}{A}, s^\sigma = \frac{S^\sigma}{A} \text{ and } \Gamma_i = \frac{n_i^\sigma}{A} \quad (13)$$

eqn (12) is written as

$$d\gamma = -s^\sigma dT - \sum_i \Gamma_i d\mu_i + \tau dp, \quad (14)$$

which is the most general form of the Gibbs adsorption equation. According to the phase rule for a system with k components in two phases, the number of independent variables ($f = k + 2 - r$, r is the number of phases) is equal to k , so, in principle, two of the $k + 2$ variables in eqn (14) can be eliminated. The elimination can be performed with the aid of the two Gibbs–Duhem relations eqn (6a), (b). With the definitions

$$s^\alpha = \frac{S^\alpha}{V^\alpha}, s^\beta = \frac{S^\beta}{V^\beta}, c_i^\alpha = \frac{n_i^\alpha}{V^\alpha} \text{ and } c_i^\beta = \frac{n_i^\beta}{V^\beta} \quad (15)$$

by eliminating dp the eqn (6a), (b) combines into

$$(s^\alpha - s^\beta)dT + \sum_{i=1}^k (c_i^\alpha - c_i^\beta)d\mu_i = 0 \quad (16)$$

If we choose the thermodynamic potential of one of the components, e.g., $i = 1$, as one of the variables to be eliminated, we get from eqn (16)

$$d\mu_1 = -\frac{s^\alpha - s^\beta}{c_1^\alpha - c_1^\beta} dT - \sum_{i=2}^k \left(\frac{c_i^\alpha - c_i^\beta}{c_1^\alpha - c_1^\beta} \right) d\mu_i \quad (17)$$

Inserting eqn (17) into eqn (14) yields the equation

$$d\gamma = -\left(s^\sigma - \Gamma_1 \frac{s^\alpha - s^\beta}{c_1^\alpha - c_1^\beta} \right) dT - \sum_{i=2}^k \left(\Gamma_i - \Gamma_1 \frac{c_i^\alpha - c_i^\beta}{c_1^\alpha - c_1^\beta} \right) d\mu_i + \tau dp, \quad (18a)$$

to be abbreviated as

$$d\gamma = -s^{(1)} dT - \sum_{i=2}^k \Gamma_i^{(1)} d\mu_i + \tau dp \quad (18b)$$

Here $s^{(1)}$ and $\Gamma_i^{(1)}$ denote the relative interfacial entropy and relative concentration of component i as defined between the brackets in eqn (18a). As a

second variable we could eliminate the pressure, *e g* , by expressing dp in T and μ 's with the aid of eqn (6a) This results in a modified form of eqn (18b) with T and $(k - 1) \mu$'s as independent variables

1.2 Gibbs' interfacial model

In reality, the transition from one homogeneous phase into another is never abrupt but gradual, extending over a certain distance (τ in Fig 1 and eqn (18b)) For example, in a system with one component (*e g* , solid/melt, Fig 2(a)) or with two components (*e g* , solid/liquid solution, Fig 2(b), (c)) the concentrations of the components will, in general, change In the interfacial model proposed by Gibbs the phases are supposed to be separated by a mathematical plane without volume -- the "Gibbs dividing surface" This implies that $\tau = 0$ and that instead of eqn (10) we have

$$V = V^\alpha + V^\beta \quad (19)$$

The two phases are assumed to continue uniformly up to this plane, and excesses or deficiencies in the extensive parameters (n_i^σ , U^σ and S^σ in eqns (7) - (9)) are attributed to the dividing surface With eqns (7), (15) and (19) the surface excess or adsorbed amount of component i per unit area becomes

$$\Gamma_i = \frac{n_i^\sigma}{A} = \frac{n_i - c_i^\alpha V + (c_i^\alpha - c_i^\beta) V^\beta}{A} \quad (20)$$

This amount is unspecified as long as the position of the dividing plane, or V^β in eqn (2), is not defined

The most common procedure for locating the dividing surface is by selecting the adsorption of one of the components to be zero, *e g* , the single component in Fig 2(a) and component 1 in Figs 2(b), (c) For $\Gamma_1 = 0$ one obtains with eqn (20)

$$V^\beta = \frac{c_1^\alpha V - n_1}{c_1^\alpha - c_1^\beta} \quad (21)$$

The introduction of eqn (21) into eqn (20) yields the so-called "relative adsorption" of component i

$$\Gamma_i^{(1)} = \frac{1}{A} \left[n_i - n_1 \left(\frac{c_i^\alpha - c_i^\beta}{c_1^\alpha - c_1^\beta} \right) + V \left(\frac{c_i^\alpha c_1^\beta - c_1^\alpha c_i^\beta}{c_1^\alpha - c_1^\beta} \right) \right] \quad (22)$$

Fig 1 System with homogeneous phases α and β separated by the transition region σ

Fig 2 Illustration of Gibbs' interfacial model (a) 1-component system, *e g* , solid/melt, (b), (c) multi-component systems, *e g* , liquid/solid with 1 = liquid solvent, 2 = solute

It may easily be shown, by eliminating V^β from the expressions, eqn (20), for Γ_1 and Γ_i , that the relative adsorption defined by eqn (22) is identical with $\Gamma_i^{(1)}$ in eqns (18a) and (b)

In the Gibbs model the adsorption, eqn (18b) reduces to

$$d\gamma = -s^{(1)}dT - \sum_{i=2}^k \Gamma_i^{(1)}d\mu_i \quad (23)$$

From this equation we get

$$\left(\frac{\partial \gamma}{\partial \mu_j} \right)_{T, \mu_{i \neq 1, j}} = -\Gamma_j^{(1)} \quad (24)$$

Remarks

(1) Within Gibbs' interfacial model an alternative means of locating the dividing plane is by taking the sum of the adsorbed amounts of all components to be zero, *i e* ,

$$\sum_{i=1}^k \Gamma_i = 0 \quad (25)$$

This leads to the so-called "reduced adsorption" values for the i components

(2) Fortunately for many systems, simplifications may be introduced in eqns (22) - (24). In solid/liquid systems the transition between the two bulk phases is often quite abrupt, and the position of the dividing surface, defined with respect to the main components in both phases, is approximately the same. Moreover the concentrations of some components will be so low that the corresponding terms (c_i^α , c_i^β) may be neglected.

(3) The well-known simple form of the Gibbs adsorption equation

$$\Gamma_j = - \frac{d\gamma}{RT \, d \ln c_j} \quad (26)$$

follows from eqn (24) under the assumptions mentioned in the previous remark for one component j in an ideal, dilute solution with

$$\mu_j = \mu_j^0 + RT \ln c_j \quad (27)$$

2 Electrical aspects [3 - 8]

2.1 Types of potentials

In the previous section we have tacitly assumed that the components were electrically neutral molecules or ions in such combination that the condition for total electrical neutrality was imposed

$$\sum n_i z_i = 0, \quad (28)$$

where z_i is the charge number of the ionic species i . As is illustrated by a simple *example* (cf. ref. 2, Ch. 8), a slight deviation of condition (28) causes a very high electrical potential — the physical reason for the high sensitivity of electrical measurements and analytical techniques based on such measurements.

Consider a single, spherical phase with a radius, r , of 1 cm placed under vacuum, e.g., a sphere of Cu or Ni with $(4/3)\pi r^3 \rho / M \approx 0.6$ moles or $0.6 N_{av} \approx 3.6 \times 10^{23}$ Cu or Ni atoms (ρ = density, M = molecular weight, N_{av} = Avogadro number). An excess charge, q , on the sphere will cause an electrical potential ψ just outside the sphere equal to

$$\psi = \frac{q}{4\pi\epsilon_0 r}, \quad (29)$$

where ϵ_0 is the permittivity of vacuum ($4\pi\epsilon_0 = 1.11 \times 10^{-10} \text{ C V}^{-1} \text{ m}^{-1}$). To obtain a potential of 1 V (at $r = 10^{-2} \text{ m}$) one needs to have an excess charge $q = 1.11 \times 10^{-12} \text{ C}$ or $1.11 \times 10^{-12}/e \approx 0.7 \times 10^7$ elementary charges, e ($e = 1.6021 \times 10^{-19} \text{ C}$). This amounts to, e.g., $3.5 \times 10^6 \text{ Cu}^{2+}$ ions or 0.6×10^{-17} moles or $3.7 \times 10^{-16} \text{ g Cu}^{2+}$.

This excess is too small to be measured with chemical analytical techniques. If the charge is located totally on the surface of the sphere it represents a fractional coverage of only about 0.3×10^{-9} (Cu^{2+} per Cu sur-

face atom) if we take the area per Cu atom at the surface to be $\sigma_a \approx 10 \text{ \AA}^2$, and thus the total number of surface atoms equals to $4\pi r^2/\sigma_a \approx 12.5 \times 10^{15}$ atoms

The example illustrates that it is possible to consider two phases of identical chemical composition but of different electrical potential. The thermodynamic potential of a charged species (ion, electron) is called the *electrochemical potential* and will be denoted as $\bar{\mu}_i$. This potential is a measurable quantity, equivalent to the μ_i 's in the previous sections. As emphasized by Gibbs [1] and Guggenheim [2], any splitting of an electrochemical potential, or a difference $\bar{\mu}_i^\alpha - \bar{\mu}_i^\beta$ between two phases, in a chemical part and an electrical part is, in principle, arbitrary and without physical significance. Electrical charges (electrons, ions) are always also chemical entities and all forces between atoms and ions are fundamentally electric in nature. However, in practice, some subdivisions have proved to be useful, notably those proposed by Lange [9]. These will briefly be summarized here, for details see refs. 6 and 7.

The electrochemical potential $\bar{\mu}_i^\alpha$, or the work done to transfer a charged particle of species i from a point infinitely distant from phase α (at potential zero) into the bulk of α , may be divided into (a) the work required for the transfer of particle i into the homogeneous volume of α deprived of charge and surface dipoles (μ_i), and (b) the work required for transfer inside a shell, representing the charge and dipoles at the interface ($z_i F\phi$, with F the faraday charge per mole of univalent ions)

$$\bar{\mu}_i^\alpha = \mu_i^\alpha + z_i F\phi^\alpha \quad (30)$$

The quantity μ_i has been termed the *chemical potential* and ϕ the *inner* or *Galvani potential*. Both are, in general, not measurable quantities. Only for two phases of the same chemical composition but different electrical potential one obtains $\bar{\mu}_i^\alpha - \bar{\mu}_i^\beta = z_i F(\phi^\alpha - \phi^\beta)$. The inner potential may be further subdivided into two components corresponding to the excess charge on the empty shell, the *outer* or *Volta potential*, ψ , and to the surface dipoles, the *surface potential* χ

$$\phi^\alpha = \psi^\alpha + \chi^\alpha \quad (31)$$

If, for the example discussed above, one plots the potential ψ as a function of the distance x from the phase α (Fig. 3) one gets, at large distances, a potential drop according to eqn. (29) with $r = (x + 1) \text{ cm}$. At short distances from the surface, contributions to the potential from short-range interactions, e.g., due to image forces and dipole interactions, will dominate. As a result it may be shown (cf. ref. 6) that at a distance $x \approx 10^{-5} \text{ cm}$, the potential is very nearly equal to the outer potential of the phase (in our example $\psi = 1 \text{ V}$). The outer potential ψ^α , defined as the work required to bring the test charge from infinity to a distance of about 10^{-5} cm from the surface of phase α , is a measurable quantity, because it is an electrical potential difference between two points in the same medium, e.g., vacuum.

Fig. 3 Electrical potential at the boundary between phase α and vacuum

Since $\bar{\mu}_i^\alpha$ and ψ^α are measurable quantities, eqns (30) and (31) enable us to introduce another measurable potential, the so-called *real potential*

$$\alpha_i^\alpha \equiv \bar{\mu}_i^\alpha - z_i F \psi^\alpha = \mu_i^\alpha + z_i F \chi^\alpha \quad (32)$$

An example of this potential is the electronic *work function*, $w = -\alpha_e^\alpha$, which is the work required to bring an electron from the interior of a phase to a point just outside the range of any surface effects, at about 10^{-5} cm away

2.2 Gibbs adsorption isotherm at charged interfaces

Solid/liquid interfaces are often charged, *e.g.*, by preferential adsorption of ions from solution or preferential dissolution of charged solid phase constituents. To satisfy the requirement of electroneutrality the countercharge must be close and the so-called electrical double layer will be formed.

The electrochemical counterpart of the Gibbs equation is most simply derived for an *ideal polarized electrode* (absence of electrode reactions, no ions, only electrons in the electrode phase α , *e.g.*, mercury/electrolyte interface), *cf.* refs 3 and 5 for details.

At constant T and p the Gibbs eqn (14) reads

$$-d\gamma = \sum_i \Gamma_i d\bar{\mu}_i, \quad (33)$$

where the Γ_i 's are the surface excesses of charged and uncharged species. The electrochemical potentials and excesses of individual ionic species are not independently variable. Electroneutrality requires that the excess of electrons in the α phase equals the total excess of positive charge in the β phase, or $\Gamma_e = \sum_i z_i \Gamma_i$, where z_i indicates the valency of ion i , including its sign. The Gibbs' equation then becomes

$$-d\gamma = + \sum_i \Gamma_i d\bar{\mu}_i^\beta + \sum_i \Gamma_i z_i d\bar{\mu}_e^\alpha \quad (34)$$

By splitting the electrochemical potentials into chemical and electrical potentials according to eqn (30), we get

$$-d\gamma = \sum_i \Gamma_i d\mu_i^\beta + \sum_i \Gamma_i z_i d\mu_e^\alpha + \sum_i \Gamma_i z_i F d(\phi^\beta - \phi^\alpha) \quad (35)$$

The quantity $F \sum \Gamma_i z_i$ may be identified with the excess charge σ on the solution side of the interface. To get a measurable potential difference instead of the unmeasurable quantity $(\phi^\beta - \phi^\alpha)$ the electrode is connected to a reference electrode. The externally measured potential difference, E , of such a cell may differ from $\phi^\beta - \phi^\alpha$ by some constant, which yields the Lippmann equation

$$-d\gamma = \sum_i \Gamma_i d\mu_i + \sigma dE, \quad (36)$$

or

$$\sigma = - \left(\frac{\partial \gamma}{\partial E} \right)_{\mu_i, T, p} \quad (36a)$$

Analogous forms of the Lippmann equation may be derived for other types of electrodes, *e.g.*, for reversible electrodes with exchange of ions between the solid and liquid phase. Very recently, Stol and de Bruyn [10] considered the case of ionic adsorption at the interface separating a sparingly soluble salt, AB, from an aqueous solution with potential determining electrolyte AY and a supporting electrolyte XY. For this system at constant T and p , eqn (33) reads

$$-d\gamma = \Gamma_{A^+} d\bar{\mu} + \Gamma_{B^-} d\bar{\mu}_{B^-} + \Gamma_{X^+} d\bar{\mu}_{X^+} + \Gamma_{Y^-} d\bar{\mu}_{Y^-} \quad (37)$$

In defining the adsorption, $\Gamma_{H_2O} = 0$ is chosen, and terms with H^+ and OH^- ions have been omitted. Using the relations

$$\mu_{AB} = \bar{\mu}_{A^+} + \bar{\mu}_{B^-} = \text{constant}, \quad (38)$$

$$\mu_{XY} = \bar{\mu}_{X^+} + \bar{\mu}_{Y^-}, \quad (39)$$

$$\mu_{AY} = \bar{\mu}_{A^+} + \bar{\mu}_{Y^-}, \quad (40)$$

and

$$\Gamma_{A^+} - \Gamma_{B^-} + \Gamma_{X^+} - \Gamma_{Y^-} = 0 \text{ (electroneutrality)} \quad (41)$$

eqn (37) may be written as

$$-d\gamma = (\Gamma_{A^+} - \Gamma_{B^-}) d\mu_{AY} + \Gamma_{X^+} d\mu_{XY} \quad (42)$$

The surface charge density is defined as the excess adsorption of lattice ions

$$\sigma \equiv F(\Gamma_{A^+} - \Gamma_{B^-}) \quad (43)$$

Inserting this definition in eqn (42) and making use of eqn (40) we get

$$-d\gamma = \frac{\sigma}{F} d\bar{\mu}_{A^+} + \frac{\sigma}{F} d\bar{\mu}_{Y^-} + \Gamma_{X^+} d\mu_{XY} \quad (44)$$

At constant ionic strength and $c_{XY} \gg c_{AY}$, eqn (42) simplifies to

$$-d\gamma = (\Gamma_{A+} - \Gamma_{B-}) d\mu_{AY} \quad (45)$$

and eqn (44) to

$$d\gamma = -\frac{\sigma}{F} d\bar{\mu}_A \quad (46)$$

Equation (45) may be integrated to find the decrease in γ if the dependence of $(\Gamma_{A+} - \Gamma_{B-})$ on μ_{AY} (*i.e.*, the adsorption isotherm) is known

If for ion A^+ equilibrium is established throughout the system we have

$$d\bar{\mu}_{A+} = d\bar{\mu}_{A+}^\beta = RT d \ln a_{A+} \quad (47a)$$

$$= d\bar{\mu}_{A+}^\alpha = F d\phi \quad (47b)$$

$$= d\bar{\mu}_{A+}^\sigma = d\mu_{A+}^\sigma + F d\psi_0, \quad (47c)$$

where $\phi = \phi^\alpha - \phi^\beta$ and ψ_0 is the average electrostatic potential at the surface relative to that of the bulk solution (β) which is arbitrarily assigned a value of zero. Substitution of eqn (47c) in eqn (46) gives

$$d\gamma = -\sigma d\psi_0 - \frac{\sigma}{F} d\mu_{A+}^\sigma \quad (48)$$

To evaluate the electrical contribution to $d\gamma$ a model for the electrical double layer has to be chosen (*e.g.*, Gouy–Chapman theory, Section 2.4), and an adsorption model for the chemical contribution, *e.g.*, that of Langmuir with

$$d\mu_i^\sigma = RT d \ln \frac{\theta}{1 - \theta}, \quad (49)$$

where θ is the fraction of the total number of sites at the interface occupied by ion i . For a review of various adsorption models see, *e.g.*, refs 5 and 8

2.3 Nernst equation, potential determining ions [11]

In general, one can distinguish among three situations for i ions as to the establishment of thermodynamic equilibrium between the bulk phases, α (solid) and β (electrolyte), and the interfacial region, σ

$$(a) \bar{\mu}_i^\alpha = \bar{\mu}_i^\sigma = \bar{\mu}_i^\beta, \quad (50a)$$

$$(b) \bar{\mu}_i^\alpha \neq \bar{\mu}_i^\sigma = \bar{\mu}_i^\beta, \quad (50b)$$

$$(c) \bar{\mu}_i^\alpha \neq \bar{\mu}_i^\sigma \neq \bar{\mu}_i^\beta \quad (50c)$$

For non-indifferent ions, *i.e.*, ions which may, in principle, take part in the solid phase and/or the interface case (c) will be an exception. The diffusion of ions in the solid phase is usually so slow that in the time of measurement no equilibrium between bulk, α , and interface, σ , is reached (case (b))

Using eqn (30) and the expression for the chemical potential of a species i in solution

$$\mu_i^\beta = \mu_i^{\beta 0} + RT \ln a_i, \quad (51)$$

where $\mu_i^{\beta 0}$ is a standard chemical potential and a_i the activity of species i (charge ze) in solution, we get for *case (a)*

$$\phi^\alpha - \phi^\beta = \frac{\mu_i^{\beta 0} - \mu_i^\alpha}{zF} + \frac{RT}{zF} \ln a_i \quad (52)$$

Since $\mu_i^{\beta 0}$ and μ_i^α may be regarded as constant, the potential changes between the bulk phases are completely determined by changes in the activity of the ion i in solution, and therefore also the measurable electromotive force, E , of a cell composed of this half-cell and a suitable reference electrode. Equation (52) is the Nernst equation, which predicts for z -valent, so-called potential-determining ions, potential changes of $59/z$ mV per decade change in a_i at 25°C . It may be remarked that for j ions, the activity a_j of which is in some way related to the activity a_i of an ion obeying eqn. (50a), $e.g.$, $\text{via } a_j \propto a_i = \text{constant}$, the Nernstian potential response also applies, even though equilibrium between the bulk phases is not established for j .

For *case b* the potential difference between the interface and the solution is given by

$$\phi^\sigma - \phi^\beta = \frac{\mu_i^{\beta 0} - \mu_i^\sigma}{zF} + \frac{RT}{zF} \ln a_i^\beta \quad (53)$$

In principle, an expression such as eqn (51) also holds for the chemical potential of species i in the interface

$$\mu_i^\sigma = \mu_i^{\sigma 0} + RT \ln a_i^\sigma \quad (54)$$

Inserting this expression in eqn (53) gives

$$\phi^\sigma - \phi^\beta = \frac{\mu_i^{\beta 0} - \mu_i^{\sigma 0}}{zF} + \frac{RT}{zF} \ln(a_i^\beta/a_i^\sigma) \quad (55)$$

The evaluation of this relation again requires knowledge of the adsorption isotherm (dependence of μ_i^σ or a_i^σ on a_i^β , cf. Section 2.2)

A special assumption is that μ_i^σ is independent of the activity of the potential determining ions in solution, which might be the case for very low surface charges/coverages, *e.g.*, for Ag^+ and I^- on AgI [11, 12]. Then the change in the potential difference between interface and solution is given by

$$d\psi^\sigma \equiv d(\phi^\sigma - \phi^\beta) = \frac{RT}{zF} d \ln a_i^\beta \quad (56)$$

If the interface potential is taken to be zero when the interface is uncharged (point of zero charge, $p.z.c.$), we get

$$\psi^\sigma = \frac{RT}{zF} \ln a_i^\beta - \frac{RT}{zF} [\ln a_i^\beta]_{p.z.c.} \quad (57)$$

The constancy of μ_i^σ implies that the change in potential across the interface due to changes in a_i^β occurs entirely between surface and solution, for case (b) (eqn (50b)) the potential difference $\phi^\alpha - \phi^\sigma$ is undefined, for case (a) (eqn (50a)) this difference is defined and constant

2.4 Gouy-Chapman-Stern model of the electrical double layer [4, 5, 7, 8]

Thermodynamics yields the relative ionic interface excesses but cannot give any information about the distribution of the ions in the double layer. The model developed by Gouy (1910) and Chapman (1913), and modified by Stern (1924) bears close resemblance to the Debye-Huckel theory for the activity coefficients in electrolytes and has been applied for the explanation of the stability of hydrophobic colloids (Derjagin-Landau-Verwey-Overbeek theory, 1945).

In the model the double layer is considered to be built up by an excess surface charge density, σ_s , on the solid electrode, and a compensating charge density of specifically adsorbed ions, σ_a , and a charge density in the diffuse part in solution σ_d . Because of electroneutrality one has

$$\sigma_s + \sigma_a + \sigma_d = 0 \quad (58)$$

An atomic picture of the double layer near to the solid surface is given in Fig. 4. The ions in solution are considered to be solvated and can approach the surface only to a distance about equal to the radius of the solvated ions (outer Helmholtz plane, OHP). In the absence of specific adsorption, the region between OHP and the surface is free of charge. When specific adsorption occurs of at least partially desolvated ions the inner region is no longer free of charge. The plane through the centers of the specifically adsorbed ions is called the inner Helmholtz plane (IHP).

The relation between the charge density in the diffuse part of the double layer and the potential difference, ϕ_d , at the OHP relative to the homogeneous bulk of the solution, is calculated in the Gouy-Chapman model by treating the ions as point charges in a dielectric continuum. The relation between the electrical potential $\phi(x)$ at a distance x from the OHP and the space charge density $\rho(x)$ is given by the Poisson equation

$$\frac{d^2\phi(x)}{dx^2} = - \frac{\rho(x)}{\epsilon_r \epsilon_0}, \quad (59)$$

where ϵ_r is the relative dielectric constant ($\epsilon_r = 78$ for water) and ϵ_0 the permittivity of vacuum ($8.854 \times 10^{-12} \text{ C V}^{-1} \text{ m}^{-1}$). The charge density, resulting from unequal concentrations, c_i , of cations and anions, is given by

$$\rho(x) = \sum_i z_i F c_i(x) \quad (60)$$

The distribution of the ions in the potential field of the double layer is described by using Boltzmann statistics

$$c_i(x) = c_{i,0} \exp\left(-\frac{z_i F \phi(x)}{RT}\right), \quad (61)$$

Fig 4 Atomic model for the ionic double layer [13]

Fig 5 Potential and charge distribution in the double layer (a) in the absence of specific adsorption, (b) with specific adsorption

where c_{i0} is the concentration of i at the point where the electrical potential is chosen to be zero (bulk of the solution). Combination of eqns (59) - (61) yields the Poisson-Boltzmann equation

$$\frac{d^2\phi(x)}{dx^2} = - \frac{F}{\epsilon_r \epsilon_0} \sum_i z_i c_{i0} \exp\left(-\frac{z_i F \phi(x)}{RT}\right) \quad (62)$$

For a symmetrical electrolyte ($z_+ = -z_- = z$, $c_{+0} = c_{-0} = c$) this equation can be solved by integrating over x with boundary conditions $\phi(x) = \phi_d$ at $x = 0$ and $\phi = 0$, $d\phi/dx = 0$ at $x = \infty$ (cf refs 4 and 5). As a result one obtains

$$\sigma_d = \int_0^\infty \rho(x) dx = -(8\epsilon_r \epsilon_0 RTc)^{1/2} \sinh\left(\frac{zF\phi_d}{2RT}\right) \quad (63)$$

For aqueous solutions at 25 °C, eqn (63) becomes

$$\sigma_d = -11\,74\,c^{1/2} \sinh(19\,46\,z\,\phi_d), \quad (64)$$

where c is in moles per liter, ϕ_d in volts and σ_d in $\mu\text{C}/\text{cm}^2$

In the absence of specific adsorption the potential distribution in the double layer is as depicted in Fig 5(a) The potential at the surface, ϕ_s , may be written as

$$\phi_s = \phi_d + \sigma_s / C_{\text{stern}}, \quad (65)$$

where C_{stern} is the capacity of the Stern layer In the presence of specific adsorption one gets a potential distribution as shown in Fig 5(b)

3 Applications

3.1 Galvanic cell

Consider a galvanic cell of type

where the left-hand half-cell is the standard hydrogen electrode and the symbol $\parallel$ indicates a liquid junction potential which, against the saturated KCl solution, may be neglected or assumed to be constant The electromotive force of the cell, $E = \phi^{\text{Cu}''} - \phi^{\text{Cu}'}$, is measurable and is written as

$$E = -\frac{1}{F} (\bar{\mu}_e^{\text{Cu}''} - \bar{\mu}_e^{\text{Cu}'}) \quad (67)$$

Thermodynamic equilibrium of electrons at interfaces 1 and 6 implies $\bar{\mu}_e^{\text{Cu}'}$ = $\bar{\mu}_e^{\text{Pt}}$ and $\bar{\mu}_e^{\text{Cu}''}$ = $\bar{\mu}_e^{\text{Ag}}$, which yields for eqn (67)

$$E = \frac{1}{F} (\bar{\mu}_e^{\text{Pt}} - \bar{\mu}_e^{\text{Ag}}) \quad (68)$$

The electrode reactions in the two half-cells are

and

Using the condition of equality of the electrochemical potentials we get

$$\bar{\mu}_e^{\text{Ag}} = \mu_{\text{Ag}} + \bar{\mu}_{\text{Cl}^-}^{\text{KCl}} - \mu_{\text{AgCl}}, \quad (71a)$$

and

$$\bar{\mu}_e^{\text{Pt}} = \frac{1}{2} \mu_{\text{H}_2}^0 - \bar{\mu}_{\text{H}^+}^0 \quad (71b)$$

Inserting these equations in eqn (68), the electromotive force becomes

$$E = \frac{1}{F} \left(\frac{1}{2} \mu_{\text{H}_2}^0 - \bar{\mu}_{\text{H}^+}^0 - \bar{\mu}_{\text{Cl}^-}^{\text{KCl}} - \mu_{\text{Ag}} + \mu_{\text{AgCl}} \right) \quad (72)$$

If we neglect the liquid junction potential between the standard hydrogen ion solution and the saturated KCl solution and use eqn (30) for the electrochemical potentials in eqn (72) we get

$$E = \frac{1}{F} \left(\frac{1}{2} \mu_{\text{H}_2}^0 - \mu_{\text{H}^+}^0 - \mu_{\text{Cl}^-}^{\text{KCl}} - \mu_{\text{Ag}} + \mu_{\text{AgCl}} \right) \quad (73)$$

It is customary to choose the electrode potential of the left-hand half-cell arbitrarily equal to zero. Thus, the tabulated standard electrode potential E^0 of the right-hand cell in fact represents

$$E_{\text{Ag}/\text{AgCl}}^0 = \frac{1}{F} (\mu_{\text{AgCl}} - \mu_{\text{Ag}} - \mu_{\text{Cl}^-}^{\text{KCl}} + \frac{1}{2} \mu_{\text{H}_2}^0 - \mu_{\text{H}^+}^0) \quad (74)$$

From eqn (71a) we get

$$\bar{\mu}_{\text{e}}^{\text{Ag}} = -FE_{\text{Ag}/\text{AgCl}}^0 + \frac{1}{2} \mu_{\text{H}_2}^0 - \mu_{\text{H}^+}^0 - F\phi^{\text{KCl}} \quad (75)$$

3.2 Oxide/electrolyte interface

With oxides direct measurement of the surface potential is not possible as with mercury and reversible surfaces. The experimental data comprise (a) material balance data (amounts adsorbed determined, e.g., by potentiometric titration) and (b) electrokinetic data (ζ -potential, coagulation studies). The electrical double layer on oxide surfaces has been investigated extensively in the last twenty years and various models have been proposed to explain the experimental results. Early potentiometric studies [14, 15] confirmed the importance of H^+ and OH^- in the establishment of the electrical double layer at the oxide/water interface, these ions being "potential-determining" (p.d.) in the sense of case (b) in Section 2.3. A summary of oxides studied until 1977 has been given by Davis *et al* [16]. Examples of more recent studies are those performed in the group of de Bruyn [17, 18]. Recent reviews and discussions of the current approaches have been presented by Dousma [18] and Westall and Hohl [19]. These approaches have been classified as "site-binding models" [18] or as "surface complexation models", since localized adsorption or surface complex formation of at least the p.d. ions is implied.

The models may be distinguished according to three aspects

(a) The specification and number of the surface sites. In the *amphoteric model* two adsorption reactions are considered to take place at the commonly accepted amphoteric site S-OH

The total number of sites available (N_s) per unit area is determined by the mass balance of the three different types of sites

$$N_s = [\text{SOH}] + [\text{SOH}_2^+] + [\text{SO}^-] \quad (78)$$

and the surface charge density

$$\sigma_s = ([\text{SOH}_2^+] - [\text{SO}^-]) F \quad (79)$$

The *two-site model* is characterized by surface reactions of the type

Two sites (S_1 and S_2) are considered, and also metal ions are assumed to take part in the surface equilibria, *e.g.*, $\text{B}_s^+ = (1/3)\text{Al}_s^{3+}$ for aluminum hydroxide, with $\text{A}_s^- = \text{OH}^-$ [17]

(b) Specific adsorption of non-p d (foreign) ions In the absence of specific adsorption the potential and charge distribution is as depicted in Fig 5(a), when specific adsorption is taken into account as in Fig 5(b)

(c) The localization of the (planes of) sites for specific adsorption In most of the proposed models the p d ions are assumed to be located in the surface plane (at potential ϕ_s in Fig 5) For the mean plane of charge and potential of the specifically adsorbed non-p d ions the IHP (ϕ_a, σ_a) as well as the surface plane have been chosen

Westall and Hohl [19] fitted five electrostatic models for the oxide/electrolyte interface to experimental data for $\gamma\text{-Al}_2\text{O}_3$ and TiO_2 . They found that all models could represent the experimental data equally well, but that the values of corresponding parameters adjusted in different models are not the same and that the models are therefore "not necessarily an accurate physical description of the interface". Westall and Hohl consider it necessary to study better defined samples, *e.g.*, latex-particles, to find the correct model. An analogous conclusion is drawn by Dousma [18], who states that for a given oxide the chemical composition and physical state of the surface have to be determined.

To give an impression of the various approaches, the amphoteric model without specific adsorption of foreign ions will be briefly described (for details see ref. 18). The two reaction equilibria, eqns (76) and (77) are characterized by the constants

$$K_1 = \frac{[\text{SOH}][\text{H}^+]_s}{[\text{SOH}_2^+]} \text{ and } K_2 = \frac{[\text{SO}^-][\text{H}^+]_s}{[\text{SOH}]} \quad (82)$$

The concentration of protons in the surface layer $[\text{H}^+]_s$ is related to the bulk concentration by the Boltzmann equation

$$[\text{H}^+]_s = [\text{H}^+] \exp(-F\phi_s/RT) \quad (83)$$

Fig 6 Calculated plots of $\sigma_s/\sigma_{\max}$ vs pH [18]
 a, e $\Delta pK = 5.6$ a - d $C_{\text{stern}} = 5 \text{ F/m}^2$
 b, f $\Delta pK = 2.0$ e - h $C_{\text{stern}} = \infty$
 c, g $\Delta pK = 0$
 d, h $\Delta pK = -2, -5, 6$ p z c pH = 9.4
 $\sigma_{\max} = 1.2 \text{ C/m}^2$
 $c = 0.1 \text{ M}$

Fig 7 Calculated plots of ϕ_s vs pH [18] $C_{\text{stern}} = \infty$, for other physical constants see Fig 6

By making use of eqns (63) and (65) of the Gouy-Chapman-Stern theory and of the electroneutrality condition

$$\sigma_s + \sigma_d = 0, \quad (84)$$

for chosen values of ϕ_d and C_{stern} , values for σ_s and ϕ_s are calculated. Subsequently, from the set of eqns (78), (79) and (82) and inserted values of σ_s , K_1 , K_2 and N_s , the concentrations of the four surface species, at % $[\text{H}^+]_s$, are determined. The pH of the solution then follows from eqn (83).

Examples of calculated plots of $\sigma_s/\sigma_{\max}$ ($\sigma_{\max} = F N_s$) and of ϕ_s vs pH are shown in Figs 6 and 7. From the model it follows that at the point of zero charge ($\sigma_s = 0$)

$$\text{pH}_{\text{pzc}} = \frac{1}{2}(\text{p}K_1 + \text{p}K_2) \quad (85)$$

Figure 6 shows that without the Stern correction $\sigma_{\max}$ is reached at relatively high pH values, and that the maximum is reached sooner for smaller values of $\Delta pK \equiv \text{p}K_2 - \text{p}K_1$. According to Fig 7, at high ΔpK the calculated curve deviates from the Nernst equation (57). For lower ΔpK values this equation is obeyed rather well, except at low pH values where charge saturation is reached.

The application of this simple amphoteric model and of more elaborate site-binding models requires knowledge of the equilibrium constants K and of parameters such as N_s (for a recent review see ref. 16).

3.3 Interface between semiconductor and oxide layer

The physical properties of the interface between a semiconductor and a thin oxide layer are largely governed by the existence of an interface barrier in the form of an excess or deficiency of charge in interface states. At surfaces or interfaces the energy states of electrons may differ from those in the interior on both sides. This has special consequences when the energy levels are located within the forbidden energy gap for bulk electrons. Electrons may become localized in these states without being able to move into the interior. Surface or interface states can have acceptor or donor character and therefore can give rise to a net surface charge density σ_{ss} per unit area that may be positive, negative or zero. The condition of electroneutrality requires that the surface charge is compensated by a charge σ_{sc} of opposite sign, distributed in a layer near the surface, the space charge layer.

$$\sigma_{ss} + \sigma_{sc} = 0 \quad (86)$$

This equation is, in principle, valid for double layers formed at various types of interfaces, *e.g.*, semiconductor/insulator systems of different kinds and semiconductor/metal contacts. The electrical field in the double layer leads to a potential difference, ϕ , with respect to the bulk of the semiconductor, which depends on the distance x from the surface ($x = 0$, see Fig. 8). In the space charge region the potential energy of electrons thus varies as $-e\phi(x)$, and the energy, $E_C(x)$, at the conduction band edge becomes

$$E_C(x) = E_C - e\phi(x), \quad (87)$$

where E_C is the bulk energy level. Similarly one has

$$E_V(x) = E_V - e\phi(x) \quad (88)$$

and

$$E_i(x) = E_i - e\phi(x), \quad (89)$$

where E_V represents the top of the valence band in the bulk and E_i is the intrinsic energy level, which is halfway between E_C and E_V . In thermodynamic equilibrium, the electrochemical potential, $\bar{\mu}_e$, or Fermi level, E_F ,

Fig. 8 Example of an energy diagram in the interfacial region of an *n*-type semiconductor

of the electrons must be everywhere the same. The distribution of electrons in the space charge region may be described by the Boltzmann equation in the form (*cf* refs 20 and 21)

$$n(x) = n_i \exp\left(\frac{E_F - E_i(x)}{kT}\right), \quad (90)$$

where n_i is the intrinsic carrier density. The same relation applies to the holes

$$p(x) = n_i \exp\left(\frac{E_i(x) - E_F}{kT}\right) \quad (91)$$

By introducing the dimensionless energy parameters [22]

$$u = \frac{E_F - E_i(x)}{kT} = u_b + \frac{e\phi(x)}{kT} \text{ and } v(x) = \frac{e\phi(x)}{kT}, \quad (92)$$

eqns (90) and (91) can be written as

$$n(x) = n_i \exp(u) = n_i \exp(u_b + v) = n_b \exp(v) \quad (93a)$$

$$p(x) = n_i \exp(-u) = n_i \exp(-u_b - v) = p_b \exp(-v), \quad (93b)$$

where n_b and p_b are the bulk concentration ($x \rightarrow \infty$). The carrier densities at the surface are given by

$$n_s = n_i \exp(u_s) = n_b \exp(v_s) \quad (94a)$$

$$p_s = n_i \exp(-u_s) = p_b \exp(-v_s) \quad (94b)$$

The space charge layers may be classified according to the relative values of the carrier concentrations at the surface, as shown in Table 1

As in Section 2.4, the relation between the electrostatic potential, ϕ , and the space charge density, ρ , is given by the Poisson equation

$$\frac{d^2\phi(x)}{dx^2} = -\frac{\rho(x)}{\epsilon}, \quad (59)$$

where ϵ is the permittivity of the semiconductor. In this case ρ is given by

TABLE 1
Classification of space charge layers

Bulk \ Space charge	n	p
Accumulation layer	$n_s > n_b$	$p_s > p_b$
Flat band	$n_s = n_b$	$p_s = p_b$
Depletion layer	$p_s < n_s < n_b$	$n_s < p_s < p_b$
Inversion layer	$p_s > n_s$	$n_s > p_s$

$$\rho(x) = e[p(x) - n(x) - N_A + N_D] , \quad (95)$$

where N_A and N_D are the concentrations of ionized acceptors and donors, which are assumed to be independent of x . Charge neutrality in the bulk yields

$$N_A - N_D = p_b - n_b \quad (96)$$

By using the dimensionless potential v , the Poisson-Boltzmann equation is obtained by combining eqns (59), (95), (96) and (93a, b) as

$$\frac{d^2 v}{dx^2} = \frac{2e^2 n_i}{\epsilon kT} [\sin h(u_b + v) - \sin h(u_b)] \quad (97)$$

The solution of this equation (see e.g., refs 21 and 22) gives the electrical field in the surface layer as a function of the surface potential

$$E = - \frac{d\phi}{dx} = \pm \frac{kT}{eL_B} F , \quad (98)$$

where

$$F = \frac{\sqrt{2}}{\{\cos h(u_b)\}^{1/2}} \{\cos h(u_b + v) - \cos h(u_b) - v \sin h(u_b)\}^{1/2} \quad (99)$$

and the Debye length, L_B , is defined by

$$L_B = \left\{ \frac{\epsilon kT}{e^2(n_b + p_b)} \right\}^{1/2} \quad (100)$$

In eqn (98) the (+) sign corresponds to $\phi < 0$ and the (-) sign to $\phi > 0$. The net charge density per unit area in the space charge layer can be expressed as

$$\sigma_{sc} (= -\sigma_{ss}) = \int_0^\infty \rho(x) dx = \epsilon \left(\frac{d\phi}{dx} \right)_{x=0} = \mp \epsilon \frac{kT}{eL_B} F_s \quad (101)$$

This means that σ_{sc} is a function of the surface potential ϕ_s . One defines a differential space charge *capacitance* as

$$C_{sc} = - \frac{d\sigma_{sc}}{d\phi_s} \quad (102)$$

The difference in densities of electrons and holes in the space charge layer with respect to the bulk can be expressed in excess quantities ΔN and ΔP defined as

$$\Delta N = \int_0^\infty (n - n_b) dx , \quad (103a)$$

$$\Delta P = \int_0^\infty (p - p_b) dx \quad (103b)$$

The difference between both excess densities yields the net space charge density

$$\sigma_{sc} = e(\Delta P - \Delta N) \quad (104)$$

By using eqns (93) and (98) these excess quantities can be numerically evaluated as a function of the surface potential and the bulk potential [20 - 22] The conductivity due to the excess carriers is called the *surface conductivity*, g_s , defined as

$$g_s = ea(\mu_{ns}\Delta N + \mu_{ps}\Delta P), \quad (105)$$

where μ_{ns} and μ_{ps} are the effective mobilities for electrons and holes in the space charge region and a is a geometrical factor In general, the values of the effective surface mobilities will be lower than the corresponding bulk values due to additional scattering centers near the surface, such as roughness and ionized impurities [21] In the case of small band bending, the effects of surface scattering on the surface conductivity can be neglected [20], and the effective mobilities at the surface can be taken equal to the bulk values

As an illustration, in Fig 9 calculated values of g_s are plotted as a function of the band bending, v_s , for two silicon samples [23] It should be noted that the dimension of the surface conductivity is $A V^{-1}$, since the excess carrier concentrations are expressed per unit surface area, g_s is often expressed in $\Omega^{-1} \square^{-1}$ (mho per square)

When a semiconductor surface, possibly covered with a thin oxide layer, is capacitively coupled to a metal electrode, the surface conductivity will change under the influence of the external field The so-called *field-effect mobility* μ_{FE} is defined by

$$\mu_{FE} = - \frac{d g_s}{d \sigma_{md}}, \quad (106)$$

Fig 9 Values of the surface conductivity g_s vs band bending v_s calculated for 5200 $\Omega \text{ cm}$ n-type and 1000 $\Omega \text{ cm}$ p-type silicon [23]

where σ_{ind} represents the total induced charge per unit area at the semiconductor surface, distributed over the interface states and the space charge region

3.4 ISFET (Ion Sensitive Field Effect Transistor) system [24]

In its simplest form this system consists of a reference electrode, a solution of unknown pH and an SiO_2/Si electrode, and is represented by

Since the bulk of the SiO_2 is considered to be a perfect insulator, between the terminals Cu'' and Cu' an arbitrary voltage, E , can be applied

$$E = \phi^{\text{Cu}''} - \phi^{\text{Cu}'} = \frac{1}{F}(\bar{\mu}_e^{\text{Cu}'} - \bar{\mu}_e^{\text{Cu}''}) \quad (108)$$

Thermodynamic equilibrium of electrons at interfaces 1 and 7 implies $\bar{\mu}_e^{\text{Cu}'} = \bar{\mu}_e^{\text{Si}}$ and $\bar{\mu}_e^{\text{Cu}''} = \bar{\mu}_e^{\text{Ag}}$, which yields for eqn (108)

$$E = \frac{1}{F}(\bar{\mu}_e^{\text{Si}} - \bar{\mu}_e^{\text{Ag}}) \quad (109)$$

The reversible reaction between the silver wire, coated with a layer of AgCl , and the saturated KCl solution has been discussed in Section 3.1

Inserting eqn (74) into eqn (109) and splitting $\bar{\mu}_e^{\text{Si}}$ into a chemical and an electrical part we get

$$E = \frac{1}{F}\mu_e^{\text{Si}} - \phi_b^{\text{Si}} + E_{\text{Ag}/\text{AgCl}}^0 + \phi^{\text{KCl}} - \frac{1}{2F}\mu_{\text{H}^+}^0 + \frac{1}{F}\mu_{\text{H}^+}^0 \quad (110)$$

The electrical potential difference between the bulk of the electrolyte (ϕ_b^{el}) and the bulk of the silicon (ϕ_b^{Si}) is considered to be composed of the following parts (see Fig. 10)

- (a) $\phi_b^{\text{Si}} - \phi_b^{\text{Si}}$, between the SiO_2/Si interface and the bulk of Si ,
- (b) $\phi_{\text{Si}}^{\text{ox}} - \phi_{\text{Si}}^{\text{Si}}$, at the SiO_2/Si interface,
- (c) $\phi_{\text{d}}^{\text{ox}} - \phi_{\text{d}}^{\text{ox}}$, across the (insulating) oxide,
- (d) $\phi_{\text{d}}^{\text{el}} - \phi_{\text{d}}^{\text{ox}}$, at the electrolyte/ SiO_2 interface due to the polarization and orientation of molecules,
- (e) $\phi_b^{\text{el}} - \phi_{\text{d}}^{\text{el}}$, between the bulk of the solution and the electrolyte/ SiO_2 interface

The charge distribution is considered to consist of three contributions: a charge on the SiO_2 surface at the electrolyte/ SiO_2 interface (σ_{ox}), and two space charges, one at the solution side (σ_{el}) and the other at the silicon side (σ_{Si}) of the SiO_2 . The charge σ_{ox} is formed by chemical interaction of the SiO_2 with the electrolyte. In this simplified model it is assumed that no charge is present inside the SiO_2 nor in the surface states at the SiO_2/Si interface.

Electroneutrality requires

$$\sigma_{\text{el}} + \sigma_{\text{ox}} + \sigma_{\text{Si}} = 0 \quad (111)$$

Fig 10 Electrical potential and charge distribution in the system electrolyte/SiO₂/Si [24]

The electrical potential differences at the interfaces 1, 5, 6 and 7 of the cell (107) retain constant values, which are determined by the chemical composition of the phases involved. As in Section 3.1 we will neglect the liquid junction potential at interface 4. With the introduced assumptions, any changes in the composition of the electrolyte, and thus in $\phi_b^{el} - \phi_d^{ox}$, and in the applied voltage E will appear completely across the SiO₂ layer as well as the space charge region in Si.

Abbreviating $(E_{Ag/AgCl}^0 - (1/2F)\mu_{H_2}^0 + (1/F)\mu_{H^+}^0)$ as $\epsilon_{Ag/AgCl}$, eqn (110) may be written as

$$E = \frac{1}{F} \mu_e^{Si} + \epsilon_{Ag/AgCl} + (\phi_b^{el} - \phi_d^{ox}) + (\phi_d^{ox} - \phi_O^{ox}) + S_1 \chi^{ox} + \phi_O^{Si} - \phi_b^{Si} \quad (112)$$

A special case of E is the voltage at which the surface potential at the silicon surface is equal to the bulk potential ($\phi_O^{Si} - \phi_b^{Si} = 0$), which is called the *flat-band voltage*, E_{FB} . When no charges are present inside the SiO₂, nor in the surface states at the SiO₂/Si interface, the potential difference $\phi_d^{ox} - \phi_O^{ox}$ is then also zero and we get

$$E_{FB} = \frac{1}{F} (\mu_e^{Si} + F S_1 \chi^{ox}) + \epsilon_{Ag/AgCl} + \phi_b^{el} - \phi_d^{ox} \quad (113)$$

In this equation $\mu_e^{Si} + F S_1 \chi^{ox}$ is equal to the negative value of the Si/SiO₂ electronic barrier energy $-\alpha_e^{Si}$ (cf. eqn (32)). Equation (113) simplifies to

$$E_{FB} = \frac{1}{F} \alpha_e^{Si} + \epsilon_{Ag/AgCl} + \phi_b^{el} - \phi_d^{ox} \quad (114)$$

For ions obeying the Nernst relation (eqns (52) or (56)) one expects E_{FB} to vary with the activity of the H⁺ ions according to

$$dE_{FB} = - \frac{RT}{F} d \ln a_{H^+}^{el} \quad (115)$$

With more complicated types of adsorption isotherms (Section 2.3) and for the site-binding models mentioned in Section 3.2, the change in E_{FB} , in general, will not simply obey the Nernst relation, but, nevertheless, can be interpreted if sufficient parameters are known (*cf* the recent calculations by Siu and Cobbold [25]). It may be remarked that for the derivation of eqn (115) it is sufficient to assume that the liquid junction potential and the charges inside the SiO_2 and in the surface states at the SiO_2/Si surface are constant and independent of $a_{H^+}^{el}$, and not necessarily equal to zero. By combining eqns (112) and (113) we get

$$E - E_{FB} = \phi_d^{ox} - \phi_o^{ox} + \phi_o^{Si} - \phi_b^{Si} \quad (116)$$

The space charge at the silicon side of the SiO_2 , σ_{Si} , is given by

$$\sigma_{Si} = -C_{ox}(\phi_d^{ox} - \phi_o^{ox}), \quad (117)$$

where C_{ox} denotes the oxide capacitance per unit area. Inserting eqn (114) into eqn (116) yields

$$E - E_{FB} = - \frac{\sigma_{Si}}{C_{ox}} + \phi_o^{Si} - \phi_b^{Si} \quad (118)$$

This equation illustrates that the surface potential and the space charge of the silicon depend on E , which is only externally variable, and on E_{FB} , which is dependent on the chemical composition of the electrolyte solution.

Experimentally the flat-band voltage E_{FB} may be determined by measuring the *differential capacitance* of the cell (*cf* eqn (102) and Fig. 9). An alternative method is to measure the *conductance* of the *inversion channel* of a MOSFET type structure, in which the metal is replaced by the electrolyte solution and the reference electrode (= ISFET). It may be shown (see refs. 24, 26, 27) that the channel conductance also varies with $(\phi_b^{el} - \phi_d^{ox})$.

An interesting *application* of the *Lippmann equation* to the semiconductor/insulator/solution system can be realized when this system behaves like an *ideal polarized electrode* [28]. As outlined in Section 3.2, in general, the surfaces of oxides will hydrolyze, resulting in the formation of surface groups of which the charge depends on the pH of the electrolyte solution. A polarizable interface can be realized, for example, by coating with a hydrophobic polymer.

For a simple 1-1 electrolyte, AB, the Lippmann equation, (36), may be written as (*cf* refs. 5, 28, 29)

$$-d\gamma = \sigma dE^\pm + \Gamma_\pm^{(H,O)} d\mu_{AB} \quad (119)$$

Here σ represents the charge density in the semiconductor phase and $E^\pm$ is the electrode potential of the semiconductor with respect to an indicator electrode reversible to cations (E^+) or anions (E^-). $\Gamma_\pm^{(H,O)}$ denotes the

relative surface excess of either anions or cations with respect to water, defined as in eqn (18a) Introducing Parsons' auxiliary function, $\zeta^\pm$ [30], which is defined by

$$\zeta^\pm = \gamma + \sigma E^\pm \quad (120)$$

one obtains by differentiating and inserting eqn (119)

$$d\zeta^\pm = E^\pm d\sigma - \Gamma_\pm^{(H_2O)} d\mu_{AB} \quad (121)$$

Cross-differentiation yields the so-called Esin and Markov coefficients

$$\left(\frac{\partial E^\pm}{\partial \mu_{AB}} \right)_{T,p,\sigma} = - \left(\frac{\partial \Gamma_\pm}{\partial \sigma} \right)_{T,p,\mu_{AB}}, \quad (122)$$

which give information about the adsorption isotherm of specifically adsorbed ions In practice, instead of an indicator electrode a reference electrode is used as in eqn (107) It may be shown [5, 29] that for such a cell, eqn (122) reads

$$- \left(\frac{\partial E}{\partial \mu_{AB}} \right)_{T,p,\sigma} = - \left(\frac{\partial \Gamma_\mp}{\partial \sigma} \right)_{T,p,\mu_{AB}} \pm \frac{1}{2F}, \quad (123)$$

where E is the potential of the reference electrode with respect to the semiconductor The left-hand side of eqn (123) can be determined as follows upon changing the electrolyte composition (μ_{AB}), the charge σ in the semiconductor (*e.g.*, the channel conductance) is kept constant by varying E In contrast with conventional polarizable electrodes, the Esin and Markov coefficients are here evaluated in a direct way, because the FET configuration enables us to determine two experimental parameters simultaneously, namely, an external voltage applied perpendicular to the Si/SiO₂ interface and the conductance parallel to this interface

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