

T 392 B 1

Contents

1. Thermodynamic Methods for the Study of Interfacial Regions in Electrochemical Systems

Roger Parsons

1. Introduction	1
2. Thermodynamics of a Single Bulk Phase Containing Charged Particles	4
3. Thermodynamics of an Interphase Containing Charged Particles	7
3.1. The Basic Equation	7
3.2. Other Forms of the Basic Equation	12
3.3. The Gibbs Adsorption Equation	14
3.4. Application of the Gibbs Adsorption Equation	16
3.5. Temperature Dependence and Enthalpies and Energies of Adsorption	17
4. Solid Phases	19
5. Specific Examples	22
5.1. Pure Metal in Contact with a Solution of a Single Salt in a Nondissociating Solvent	22
5.2. Pure Metal in Contact with a Solution of Two Salts in a Solvent	28
5.3. Pure Metal in Contact with a Solution of an Electrolyte and a Nonelectrolyte in a Solvent	32
5.4. Binary Alloy in Contact with a Solution of a Single Electrolyte	33
5.5. Binary Alloy in Contact with a Solution of Two Electrolytes	35
5.6. Semiconducting Phase in Contact with an Electrolyte	36
5.7. Nonionic, Nonconducting Phase in Contact with an Electrolyte	36
5.8. Pure Ionic Solid in Contact with an Electrolyte Containing One of its Constituent Ions: $1A + KA + S MX$	36
5.9. Ionic Crystal Containing Two Species in Solid Solution in Contact with an Electrolyte Containing One of the Constituent Ions: $MA + KA + S MX + NX$	37

5.10. Ion-Exchange Membrane in Contact with a Binary Electrolyte: MA + KA + S MX + KX	38
5.11. Three-Phase Electrode, in which a Gaseous Component is in Equilibrium with a Component in Solution	38
5.12. Electrode with a Surface Species in Equilibrium with, but not Present in, a Bulk Phase	41
6. Partial Dissociation and Partial Charge Transfer	42
References	43

2. The Electrode Potential

Sergio Trasatti

1. Introduction	45
2. Components of the Electrode Potential	47
2.1. Bulk Structure of Metals	47
2.2. The Surface of Metals	50
2.3. The Surface of Liquid Polar Phases	55
2.4. Metal-Metal Contact	56
3. Origin of the Electrode Potential	60
3.1. Electrons in Liquid Polar Phases	60
3.2. Metal-Polar-Liquid Contact	62
3.3. Electron Work Function of Metals in Polar Liquids	65
4. Meaning of Measured Potentials	69
4.1. Measurement of Potentials	69
4.2. Relative Electrode Potential	70
4.3. Single Electrode Potential	71
4.4. Absolute Electrode Potential	72
4.5. Meaning of Potential in Terms of Electrode Reaction	77
References	78

3. The Double Layer in the Absence of Specific Adsorption

R. Reeves

1. Introduction	83
2. Experiment Techniques and Some Useful Relationships and Definitions	84
3. Introduction to the Use of Models to Describe the Double Layer	100
4. Diffuse Layer Theory and Its Validity	105
4.1. Fundamental Theory	105
4.2. Applications of the Simple Theory	110
5. Some Proofs, Limitations, and Possible Extensions of Diffuse Layer Theory	114
6. Models of the Inner Layer in the Absence of Specific Ionic Adsorption	124
References	132

4. Specific Adsorption of Ions

M. A. Habib and J. O'M. Bockris

1. Introduction	135
2. Definition	136

2.1. Introduction	136
2.2. Definition in Terms of Gibbs Surface Excess	137
2.3. Superequivalent Adsorption	138
2.4. Contact Adsorption	138
3. History of Specific Adsorption	139
4. Phenomenology of Specific Adsorption	141
5. Determinations of Specific Adsorption	144
5.1. Quasithermodynamic Methods	144
5.2. Discussion of the Electrocapillary Thermodynamics	152
5.3. Direct Methods	154
5.4. Method Based on Measurement of Surface Tension at Solid Metals	160
6. Comparison of Different Methods for the Measurement of Specific Adsorption	162
6.1. A Comparison of the Electrocapillary and Capacitance Integration Methods to Obtain Surface Tension	162
6.2. Comparison of Results Obtained by Electrocapillary, Ellipsometry, and Radiotracer Methods	172
7. The Validity of Diffuse Layer Theory	175
8. Effect of the Neglect of Γ_{H_2O}	179
9. Partial Charge Transfer in Specific Adsorption	180
9.1. Introduction	180
9.2. The Work of Lorenz and Co-Workers	181
9.3. Discussion on Lorenz's Determination of Partial Charge	182
9.4. The Work of Vetter and Schultze	183
9.5. Summary	186
10. Forces Involved in Specific Adsorption	186
11. The Isotherms for Ionic Adsorption	189
11.1. General	189
11.2. The Single-Imaging Isotherm	191
11.3. Multiple-Imaging Isotherm	201
11.4. Conclusion	202
12. Specific Adsorption and Solvation	203
12.1. General	203
12.2. Conclusion	205
13. Simultaneous Specific Adsorption of Anions and Cations	205
13.1. Introduction	205
13.2. The Method of Delahay and Co-Workers	206
13.3. The Method of Hurwitz and of Parsons and Co-Workers	209
13.4. Discussion	211
References	213

5. Potentials of Zero Charge

A. N. Frumkin, O. A. Petrii, and B. B. Damaskin

1. Introduction	221
2. The Notion of the Electrode Charge	222
3. Methods of Determination of the Potentials of Zero Charge	227
3.1. Direct Determination of the Value or Sign of the Surface Charge	227

3.2. Development of Electrodes with Zero Charge	229
3.3. Electrocapillary Methods	231
3.4. Adsorption Methods	235
3.5. Methods Based on the Dependence of the Properties of the Diffuse Part of the Double Layer on the Surface Charge	239
4. Influence of Metal Nature, Solution Composition, and pH on the Potentials of Zero Charge	246
5. Potentials of Zero Charge and the Adsorption of Organic Compounds on Electrodes	259
6. Potentials of Zero Charge and the Nature of the Medium	267
6.1. Metal/Vacuum Interface	267
6.2. Metal/Nonaqueous Solution Interface	274
6.3. Metal/Electrolyte Melt Interface	277
6.4. Metal/Solid Electrolyte Interface	282
7. Potentials of Zero Charge and Electrochemical Kinetics	282
8. Conclusions	285
References	285

6. Electric Double Layer on Semiconductor Electrodes

Yu. V. Pleskov

1. Introduction	291
2. The Theory of Double Layer on Semiconductor Electrodes	293
2.1. Charge and Potential Distribution	293
2.2. Surface Conductivity	298
2.3. Differential Capacity	301
2.4. Surface States	302
3. The Semiconductor-Electrolyte Interface at Quasiequilibrium	306
3.1. Relaxation Characteristics of Space Charge and Surface States	306
3.2. Photopotential	309
4. Distinctive Features of the Experimental Study of Semiconductor Electrodes	311
4.1. Basic Methods	311
4.2. Some Details of Experimental Techniques	312
5. Structure of the Double Layer on Semiconductor Electrodes	312
5.1. Space Charge	312
5.2. The Helmholtz Layer	319
5.3. Fast Surface States	323
6. Conclusions	325
References	327

7. Insulator/Electrolyte Interface

L. I. Boguslavsky

1. Introduction	329
2. Concerning Differences between Insulating and Metal Electrodes	330

3. Thermodynamic Approach to the Insulator/Electrolyte Interface	332
4. Determination of the Potential due to Adsorbed Iodine at the Anthracene Electrode	335
5. Electrochemical Injection and the Exchange Currents Occurring on the Insulating Electrodes	339
6. Photoelectrochemical Processes on the Insulating Electrodes	345
7. Reactions of Excitons at the Insulator/Electrolyte Interface	347
8. Photosensitized Reactions with Participation of Excited Molecules in the Electrolyte	349
9. Conclusion	351
References	351

8. The Adsorption of Organic Molecules

B. B. Damaskin and V. E. Kazarinov

1. Introduction	353
2. Reversible Adsorption of Organic Substances	354
2.1. Qualitative Relationships of Reversible Adsorption of Organic Substances on Ideally Polarizable Electrodes	354
2.2. Thermodynamics of Surface Phenomena in the Case of Adsorption of Organic Substances on an Ideally Polarizable Electrode	360
2.3. Phenomenological Description with the Use of Macromodels of the Reversible Adsorption of Organic Substances on Electrodes	369
2.4. The Molecular Theory of Adsorption of Organic Compounds on Electrodes	378
3. Irreversible Adsorption of Organic Substances	381
3.1. General Regularities of the Adsorption of Organic Substances on Catalytically Active Electrodes	381
3.2. Adsorption of Methanol on Platinum	385
3.3. Adsorption on Platinum of Other Organic Compounds	388
References	391

9. The Double Layer in Colloidal Systems

Robert John Hunter

1. Charge and Potential Distribution at Interfaces	397
1.1. Potential Distribution in the Double Layer	397
1.2. Simultaneous Charge and Potential Measurements on the Double Layer	401
2. Electrokinetic Phenomena	404
2.1. The Electrokinetic (ζ) Potential	404
2.2. Electro-osmosis	405
2.3. Streaming Potential	409
2.4. Electrophoresis	412
2.5. Position of the Plane of Shear	416
2.6. Electroviscous Effects	417

3. The Double Layer in Colloid Stability	420
3.1. Coagulation Behavior of Electrostatically Stabilized Sols	420
3.2. Total Potential Energy of Interaction between Particles	422
3.3. The Potential Energy of Repulsion	423
3.4. The Potential Energy of Attraction	428
3.5. Experimental Tests of the DLVO Theory	430
4. Concluding Remarks	433
References	434
 <i>Annotated Author Index</i>	 439
<i>Subject Index</i>	445

1

Thermodynamic Methods for the Study of Interfacial Regions in Electrochemical Systems

ROGER PARSONS

1. Introduction

Thermodynamics is concerned with the relations between the observable properties of macroscopic pieces of matter. It is essentially an empirical science based on accumulated experience of the behavior of real systems. Its great utility is due to the fact that it enables information derived from experiment to be presented in a form which may be more readily understandable than the experimental results themselves. This transformation of information may be done without a detailed knowledge of the structure of the system being studied. Conversely, if no information about structure is contained in the original experimental data, no such information can be obtained by the operation of thermodynamic transformations on these data.

This chapter is concerned with the deduction of information about the composition of interfacial regions from a property such as the interfacial tension in a liquid system together with a knowledge of the equilibrium properties of the adjoining bulk phases. This particular transformation of information may be claimed as the most remarkable of the applications of classical thermodynamics. The technique by which this may be carried out was developed

ROGER PARSONS • Laboratoire d'Electrochimie Interfaciale du C.N.R.S., 92190 Meudon, France.

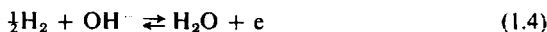
first by Gibbs⁽¹⁾ in 1878 in his comprehensive paper "On the Equilibrium of Heterogeneous Substances." He used the device of representing the real system (which consists of two bulk phases with an *interphase* between them) by an equivalent system in which the properties of the adjoining phases remain constant up to a mathematical plane, the *interface*, separating them. All differences of properties between the real system and this model system were then ascribed to the interface. This approach is often considered to be too abstract and certainly runs into difficulties when the interphase is curved or not at equilibrium.⁽²⁾ Nevertheless, for a plane interphase, at equilibrium, the deductions from the Gibbs model are identical with those made from a model using an interfacial region of finite thickness,^(3,4) and there is good reason to believe that they are completely correct. Gibbs' method was devised with great ingenuity at a time when little was known about the real thickness of interfacial regions and it is independent of this knowledge. However, the finite interphase method is probably easier to understand, as well as being capable of wider application; consequently this approach will be used in the present chapter.

The use of a model having an interphase of finite thickness also has advantages in the discussion of systems containing charged particles because of the long-range character of electrostatic forces. The region of inhomogeneity in such systems thus tends to be of greater extent than in the absence of particles carrying a net electric charge. It is possible for these inhomogeneous regions to become macroscopic, if the phases are poor conductors or if macroscopic pieces of matter carry finite charge. Under the latter condition the forces between pieces of charged matter become very large indeed, as illustrated dramatically by Feynman.⁽⁵⁾ It is unusual to carry out electrochemical experiments using pieces of matter which bear a net charge, partly because large energies are required to create these charges. Consequently, it will be assumed here that there is no *macroscopic* separation of charge, although of course there is often free movement of charge within a phase as well as across an interphase.

Although Gibbs provided the basic foundation for the thermodynamic interpretation of interfacial phenomena, the application of his principles to charged interfaces has been the subject of much discussion in particular situations. In fact, the equation summarizing the most important characteristic of an electrochemical interphase was derived by Lippmann⁽⁶⁾ even before Gibbs' work was published [Eq. (3.72)]. His derivation assumed that no charge transfer across the interface occurs; this situation has come to be known as an *ideal polarized* or *blocked* interface. The distinction between the ideal polarized interface and other types of interface, across which charge transfer can occur, has led to some controversy as to whether there is a difference in kind, or merely a difference in degree. In fact, the different points of view lead to the same practical results; an illustration of the lack of dependence of thermodynamics on the model adopted. Frumkin⁽⁷⁾ seems to have been the first to show clearly that the ideal polarized interface is a limiting case of the interface with charge transfer. Later, Grahame⁽⁸⁾ showed, in an illustrative and quantitative way, the reasons for the

existence of this limiting case, although in his thermodynamic analysis⁽⁹⁾ he followed to a large extent the work of Koenig,⁽¹⁰⁾ who assumed the existence of a physical barrier to charge transfer.

The reasons for the absence of finite charge transfer may be illustrated by considering, as an example, mercury in contact with aqueous KCl. The possible reactions which would transfer charge across the interphase are



each reaction being written in the standard way with the electron on the right-hand side. From the Nernst equation and the known standard electrode potentials, it is possible to calculate the concentration of the minority component in each couple at any given electrode potential. This has been done in Table 1 for two potentials, -0.2 and 0.8 V, with respect to the hydrogen electrode potential; the activities of Hg, KCl, and H_2O were assumed to be unity for each reaction. From these results it is then possible to find the charge required to change the concentration of the minority species from its equilibrium value at -0.2 V to the equilibrium value at -0.8 V if an assumption is made about the volume of the bulk phases. Here it is assumed that the volume of each bulk phase is 10^{-4} m^3 (100 cm^3). This charge is tabulated in the last column of Table 1. It is immediately evident that for the first three species the charge is extremely small and probably undetectable in a normal experiment. Reactions (1.1), (1.2), and (1.3) are fast reactions and this estimate is reliable. In contrast, reaction (1.4) is a very slow reaction at this interface and it will not come to equilibrium in the normal time scale. At -0.8 V the current due to this reaction would be about 0.04 A m^{-2} . This is sufficiently small for its effect on the interfacial properties to be neglected. This example illustrates the thermodynamic [reactions (1.1), (1.2), (1.3)] and kinetic [reaction (1.4)] reasons for the absence of significant charge transfer. It confirms the view that the ideal polarized interface is a limiting case,

Table 1

Equilibrium Concentration of Species at the Interface Hg|KCl + H_2O at Two Different Potentials at 25°C and the Charge Required to Form These Quantities in a Volume of 10^{-4} m^3

Concentration of minority species	E^H/V		Q/C
	-0.2V	-0.8V	
$[\text{Hg}_2^{2+}]/\text{mol m}^{-3}$	3.6×10^{-45}	1.9×10^{-63}	6.9×10^{-44}
$[\text{K}(\text{Hg})]/\text{mol m}^{-3}$	5×10^{-24}	7×10^{-14}	6.7×10^{-13}
$P_{\text{Cl}_2}/\text{atm}$	1.8×10^{-64}	9.5×10^{-85}	1.5×10^{-61}
$P_{\text{H}_2}/\text{atm}$	5.8×10^6	1.11×10^{27}	9.6×10^{29}

not one for which some special mechanism must be invoked. In spite of this, it is not incorrect to carry out the thermodynamic analysis as if there were a "barrier" at the interface which permits no charge to cross.

It is important to note that the concept of the ideal polarized interface includes the case where a local transfer of charge can take place. For example, on a platinum electrode at potentials up to about 300 mV positive of the equilibrium hydrogen potential, hydrogen ions from the solution adsorb, reacting with electrons from the metal to form essentially neutral hydrogen atoms. This reaction which may be represented as



is fast on platinum and so may be assumed to be in equilibrium except on very short time scales. Although (1.5) is a charge transfer reaction, it does not result in the net transfer of charge from one bulk phase to the other, as do reactions (1.4)–(1.4). From the point of view of the externally observable parameters which are used in a thermodynamic analysis, there is no distinction between the adsorption of H^+ in the ionic form or in the atomic form, because the difference lies in the location of the charge within the interphase. This limiting case of charge transfer can in fact be identified by other methods and it was clearly recognized by Frumkin and his colleagues in their study of the platinum electrode in the 1930s.⁽¹¹⁾ However, the concept of a partial charge transfer and the way in which it enters the thermodynamic relations was enunciated by Lorenz and his co-workers from 1961.⁽¹²⁾

In this chapter the derivation of the thermodynamic relations will be made using the minimum of assumptions about the physical nature of the system. Specific assumptions may then be introduced in order to apply this more general treatment to specific physical situations, where other evidence indicates the nature of the interphase. Thus the general treatment of Sections 2 and 3 is followed by a series of more specific examples in Section 4 which illustrate the application of the thermodynamic method.

2. Thermodynamics of a Single Bulk Phase Containing Charged Particles

At first sight the simplest expression for the energy U of the bulk region of a single phase which may undergo thermal, mechanical, and matter exchange with its surroundings is

$$dU = T dS - p dV + \sum_i \bar{\mu}_i dm_i \quad (2.1)$$

where T is the temperature, S the entropy, p the pressure, V the volume, m_i the amount of species i in the phase, $\bar{\mu}_i$ is the electrochemical potential of species i if it carries a charge and the chemical potential if it carries no charge. The summation in Eq. (2.1) includes all independent components in the phase; that is, all

species whose concentration may be varied independently. It is usual to include ionic species or electrons separately in this summation and then to impose additionally the electroneutrality condition

$$\sum_i z_i m_i = 0 \quad (2.2)$$

since, as discussed above, only electrically neutral systems occur under normal conditions. The imposition of (2.2) allows any range of composition of positively and negatively charged particles provided that there is not an excess of charge of one sign.

However, the incorporation of Eq. (2.2) into Eq. (2.1) in a general way is cumbersome starting from the concept of ions as independent components, particularly when partial dissociation of some species exists in the system. Much of this difficulty can be avoided by adopting a more operational approach in terms of the amounts of species actually added to the phase when it is prepared. These are always uncharged species, metals in an alloy or "salts" in an electrolyte (the term "salt" here includes any neutral combination of ions such as an acid or a base as well as a conventional salt). Consequently, (2.1) may be replaced by

$$dU = T dS - p dV + \sum_j \sum_k \mu_{j,k} dm_{j,k} \quad (2.3)$$

where $\mu_{j,k}$ is the chemical potential of an uncharged species present in an amount $m_{j,k}$. The sum is then over all components of the phase as defined in conventional thermodynamics, which is one less than the sum in Eq. (2.1). It is evident that this reduction in the number of components is a result of the fact that (2.3) includes the electroneutrality condition; in other words, (2.3) is a solution for (2.1) and (2.2). The species indicated by the subscript j, k may be a species which does not dissociate into ions or one which dissociates into two or more kinds of ions. Strictly speaking, therefore, a varying number of subscripts would be required to indicate these possibilities. The use of two subscripts covers the commonest case of two kinds of ions. Nondissociating species will be indicated by putting $k = 0$. It will be assumed that there are J types of cations, K types of neutral species and $J_0 - J$ types of nondissociating species. Thus the summation covers the range $1 < j < J_0$, $0 < k < K$ although not every combination of cation and anion is necessarily present; some of the $m_{j,k}$ may be zero.

If the species denoted by the subscript j, k dissociates into species carrying z_j , z_k unit charges, this species may be regarded as being composed of $\nu_{j,k}$ positively charged particles and $\nu_{k,j}$ negatively charged particles. In metallic phases $\nu_{j,k} = 1$ and $\nu_{k,j} = z_j$, the number of electrons assumed to be produced by each metal atom (this number is arbitrary and may be taken as 1 or the conventional valency of the metal without affecting the thermodynamic argument). However, in electrolytes the relation between the charge number and the number of ions in the salt is not quite so simple, although it must always satisfy the

$$z_j \nu_{k,j} = -z_k \nu_{j,k} \quad (2.4)$$

A given ion may be present in more than one salt so that the relation between the m_i in Eq. (2.1) and the $m_{j,k}$ in Eq. (2.3) has the form

$$m_i = \sum_{k=1}^{K} \nu_{i,k} m_{j,k} \quad (2.5)$$

for the cations, or

$$m_i = \sum_{j=1}^J \nu_{i,j} m_{j,k} \quad (2.6)$$

and

$$m_i = m_{j,0} \quad (2.7)$$

for the nondissociating species. There are consequently $J_0 + K$ chemical species present in the phase, which as a result of the electroneutrality condition correspond to $J_0 + K - 1$ components.

It is convenient to define thermodynamic functions other than the energy. For a bulk phase, these are the enthalpy, H , the Helmholtz energy, A , and the Gibbs energy, G . These are defined by

$$H = U + pV \quad (2.8)$$

$$A = U - TS \quad (2.9)$$

$$G = H - TS \quad (2.10)$$

and it then follows from Eq. (2.3) that

$$dH = T dS + V dp + \sum_{j=1}^{J_0} \sum_{k=0}^K \mu_{j,k} dm_{j,k} \quad (2.11)$$

$$dA = -S dT - p dV + \sum_{j=1}^{J_0} \sum_{k=0}^K \mu_{j,k} dm_{j,k} \quad (2.12)$$

$$dG = -S dT + V dp + \sum_{j=1}^{J_0} \sum_{k=0}^K \mu_{j,k} dm_{j,k} \quad (2.13)$$

It is frequently convenient to express the equilibrium condition for a bulk phase in terms of the variation of the intensive variables. Since Eq. (2.3) is a complete differential, the standard technique of integrating with respect to the extensive variables to yield

$$U = TS - pV + \sum_{j=1}^{J_0} \sum_{k=0}^K \mu_{j,k} m_{j,k} \quad (2.14)$$

then differentiating

$$dU = T dS + S dT - p dV - V dp + \sum_{j=1}^{J_0} \sum_{k=0}^K (\mu_{j,k} dm_{j,k} + m_{j,k} d\mu_{j,k}) \quad (2.15)$$

and finally, comparing (2.15) with (2.3) yields

$$S dT - V dp + \sum_{j=1}^{j=J_0} \sum_{k=0}^{k=K} m_{j,k} d\mu_{j,k} = 0 \quad (2.16)$$

This is the Gibbs–Duhem equation for this bulk phase.

3. Thermodynamics of an Interphase Containing Charged Particles

3.1. The Basic Equation

An interphase may be treated in a similar way to a bulk phase except that its dimension in one direction is very small, being perhaps a few molecular diameters, and the properties vary marked with position in this direction. Provided that the radius of curvature is large, the interphase may be regarded as plane and its energy then differs from that of a bulk phase by a term expressing the contribution of changes of energy due to a change of the area of contact, A_s , of the two phases. For a liquid/liquid interface, this energy contribution is γdA_s , where γ is the interfacial tension ("edge" effects are eliminated by considering a section of an interface in a larger system). Thus the energy is written as

$$dU^\sigma = T dS^\sigma - p dV^\sigma + \gamma dA_s + \sum_{j=1}^{j=J_0} \sum_{k=0}^{k=K} \mu_{j,k} dm_{j,k}^\sigma \quad (3.1)$$

where the superscript σ indicates interfacial properties; since the intensive variables, T , p , and the $\mu_{j,k}$ are uniform through a system at equilibrium, no subscript is necessary for them.

The amounts of matter in the interphase, $m_{j,k}^\sigma$, differ from those in a bulk phase in that they are usually far from uniformly distributed in the direction perpendicular to the interface. In an equilibrium system the density of each substance is uniform in the directions parallel to the interface. The nonuniformity perpendicular to the interface does not prevent a discussion of this problem in terms of equations like (3.1), but it may require special discussion when some of the species present in one of the adjoining phases are not present in the other. The way in which this may occur for charged species has been discussed in Section 1 for the ideal polarized electrode. This situation may affect the number of independent variables in the system of two phases with the intervening interphase. It is therefore necessary to discuss the variance of such a system.

In a system of two phases α and β which contain, respectively, a and b components, it follows from (2.16) that there are $a + b + 4$ independent intensive variables when the phases are separate. However, the existence of two equations like (2.16) means that the variance of the two separate phases is $a + b + 2$. When the two phases are brought into contact and allowed to equilibrate this system as a whole is subject to a number of equilibrium conditions. If no component is common to both phases the additional conditions are

thermal equilibrium, hydrostatic equilibrium, and electrostatic equilibrium. The first and second conditions are expressed by the equality of temperature and pressure of the two phases and the (plane) interphase. The third condition means that there is a single electroneutrality condition for the system as a whole in place of the two electroneutrality conditions for the two phases separately. Thus in fact only one degree of freedom is eliminated and $a + b + 3$ intensive variables remain. With the two Gibbs–Duhem equations for the separate phases this means that the variance is $a + b + 1$.

Charge transfer between the two phases may occur in two ways, either by oxidation–reduction reactions, like $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+} + e$, between components which are present in only one phase, or by the transfer of a charged component from one phase to the other, like $\text{Fe}^{2+}(\text{m}) \rightleftharpoons \text{Fe}^{2+}(\text{s})$. If there are q types of charge transfer reaction of the first kind, then there are q equilibrium conditions and the variance is reduced to $a + b + 1 - q$. The second kind of charge transfer requires the presence of components common to both phases. If there are c such components then there are $a' + c = a$ components in phase α and $b' + c = b$ components in phase β . In the two phases separately there are then $a' + b' + 2c + 4$ intensive variables which on contact are reduced by 3 according to the thermal, hydrostatic, electrostatic, and Gibbs–Duhem conditions described above, but also by c conditions because of the identity of the c component in the two phases. The variance thus becomes $a' + b' + c + 1$, and in general for both kinds of charge transfer equilibrium and for the absence of charge transfer equilibrium the variance is $C + 1 - q$, where C is the total number of components in the two-phase system as a whole, the components being defined as neutral species in the way described in the previous section. If ionic components (described by m_i) are chosen the total number will be $C' = C + 2$ and the variance is then $C' - 1 - q$. The summation in Eq. (3.1) will then consist of $C - 1 - q$ (or $C' - 3 - q$) independent terms whereas it is written with C terms.

In the simplest example of a nonpolarizable interface there is one method of charge transfer and $q = 0$ or 1, the dependent terms are then eliminated by using the Gibbs–Duhem equation for the two bulk phases. If $q > 1$ there are relations between chemical potentials of species within each phase due to the oxidation–reduction equilibrium. The presence of such multiple equilibria does not bring any new features to the interfacial problem and it will not be discussed further here.

When charge transfer across the interphase occurs by only one species of reaction, it is convenient to separate the sum in Eq. (3.1) into two parts corresponding to the two phases adjoining the interphase. Many such systems are composed of an electronic conductor α and an ionic conductor β ; for such a system (3.1) may be written

$$dU^\sigma = T dS^\sigma - p dV^\sigma + \gamma dA_s + \sum_{j=1}^{j=J_0^\alpha} \mu_{j,\alpha}^\alpha dm_{j,\alpha} + \sum_{j=1}^{j=J_0^\beta} \sum_{k=0}^{k=K} \mu_{j,k}^\beta dm_{j,k} \quad (3.2)$$

since electrons are the only negatively charged species which need to be considered in phase α and no uncharged component j, k is common to both phases.

This equation may be used in this form; if this is done the potential difference E across the interface (measured with respect to an electrode reversible with respect to an ionic species in phase β) is a dependent variable, controlled by the charge transfer equilibrium across the interface. On the other hand, it is also useful to introduce this charge transfer equilibrium explicitly and to replace one of the chemical potentials with the electrical potential. In order to do this, it is necessary also to specify the ion in phase β to which the reference electrode is reversible. It will be assumed here that this is the ion N, which for convenience is taken to be an anion, while the equilibrium reaction in the interphase under study involves the cation M. The assumption that M and N have charges of different sign is not necessary; they may both be cations or both anions. However, if M and N are identical, it follows immediately that E is zero or constant and no useful information can be obtained by using this quantity.

If the interfacial reaction consists of the transfer of the ion M^{z+} between the phases, the equilibrium condition is

$$\bar{\mu}_{M^{z+}}^{\alpha} = \bar{\mu}_{M^{z+}}^{\beta} \quad (3.3)$$

which may also be written

$$\mu_M^{\alpha} - z_M \bar{\mu}_o^{\alpha} = \mu_{M,N}^{\beta} - (z_M/z_N) \bar{\mu}_N^{\beta} \quad (3.4)$$

whence

$$z_M (\bar{\mu}_N^{\beta}/z_N - \bar{\mu}_o^{\alpha}) = \mu_{M,N}^{\beta} - \mu_M^{\alpha} \quad (3.5)$$

The quantity in brackets on the left-hand side of (3.5) will be defined as $F\epsilon$, where F is Faraday's constant. ϵ is a quantity directly related to the potential difference E between the terminals of the cell by the relation

$$\epsilon = E + K \quad (3.6)$$

where K is a sum of chemical potentials of the components of the reference electrode and is independent of the composition of the phases α and β . Thus

$$z_M F \epsilon = \mu_{M,N}^{\beta} - \mu_M^{\alpha} \quad (3.7)$$

The terms in the species M, N and M may then be extracted from (3.2),

$$\mu_M^{\alpha} dm_M^{\alpha} + u_{M,N}^{\beta} dm_{M,N}^{\beta} \quad (3.8)$$

and in view of (3.7) may be rewritten in the form

$$-z_M F \epsilon dm_M^{\alpha} + \mu_{M,N}^{\beta} d(m_M^{\alpha} + m_{M,N}^{\beta}) \quad (3.9)$$

The second term may be regarded as expressing the change in energy consequent on a change of the total amount of M^{z+} in the interphase, which can be denoted by $m_{\Sigma M}^{\alpha}$,

$$-z_M F \epsilon dm_M^{\alpha} + \mu_{M,N}^{\beta} dm_{\Sigma M}^{\alpha} \quad (3.10)$$

Note that in writing (3.4) it has been implicitly assumed that M, N is the only species containing M in phase β . (This assumption can be dropped at the expense of some further algebra.) The total amount of M in the interphase is a well-defined quantity independent of the state of the charge transfer reaction, or the distribution of charge in the interphase. However, m_M^σ is not so well defined because the amount of M (as metal atoms) does depend on the state of the charge transfer reaction. If it is *assumed* that the charge distribution in the interphase can be expressed in terms of an excess or deficiency of electrons on the side of the interphase adjoining phase α and a deficiency or excess of N ions on the side adjoining phase β , this may be related to m_N^σ . Since all other components are considered to be present always in electrically neutral groups j, k , then $z_M m_M^\sigma$ may be taken to represent the excess of electrons on the phase α side of the interphase. This contributes a charge Q^α given by

$$Q^\alpha = -z_M F m_M^\sigma \quad (3.11)$$

This is necessarily equal and opposite to the charge on the phase β side of the interphase represented by the N ions:

$$Q^\beta = -Q^\alpha = z_N F m_N^\sigma \quad (3.12)$$

It must be noted first that this definition of charge has a formal character and second that it depends on the nature of the ion N to which the reference electrode is reversible, because this affects the division of the total amount of M^{z+} in the interphase into a part on the α side of the interphase and a part on the β side.

The full equation (3.2) may now be written in the form

$$dU^\sigma = T dS^\sigma - p dV^\sigma + \gamma dA_s \sum_{j=1}^{j=J^\alpha-1} \mu_{j,e}^\alpha dm_{j,e}^\sigma + \sum_{j=J^\alpha+1}^{j=J^\beta-1} \sum_{k=0}^{k=K-1} \mu_{j,k}^\beta dm_{j,k}^\alpha + \varepsilon dQ^\alpha + \mu_{M,N} dm_{\Sigma M}^\sigma \quad (3.13)$$

A similar modification can be made if the interfacial reaction is an oxidation-reduction reaction, represented by



The equilibrium condition is

$$\tilde{\mu}_{M^{z+}}^\beta = \tilde{\mu}_{M^{(z+1)+}}^\beta + \tilde{\mu}_e^\alpha \quad (3.15)$$

which may be written

$$\mu_{M^{z+},N}^\beta + \tilde{\mu}_e^\alpha = \mu_{M^{(z+1)+},N}^\beta - \tilde{\mu}_N^\beta / z_N \quad (3.16)$$

where N is again the ion (assumed to be an anion) in equilibrium with the reference electrode. Thus

$$F\varepsilon = (-\tilde{\mu}_N^\beta / z_N - \tilde{\mu}_e^\alpha) = \mu_{M^{z+},N}^\beta - \mu_{M^{(z+1)+},N}^\beta \quad (3.17)$$

The terms extracted from (3.2) are now

$$\tilde{\mu}_{M^{z+},N}^\beta dm_{M^{z+},N}^\sigma + \tilde{\mu}_{M^{(z+1)+},N}^\beta dm_{M^{(z+1)+},N}^\sigma \quad (3.18)$$

which with (3.17) may be written

$$-F\varepsilon dm_{M^{(z+1)+,N}}^{\alpha} + \mu_{M^{z+},N}^{\beta} dm_{\Sigma M}^{\sigma} \quad (3.19)$$

where it is assumed that the ion M exists in the interphase only in the two forms taking part in the oxidation-reduction reaction (3.14). Thus again in (3.19) the second term represents the effect on the energy of variation in the total amount of M in the interphase. The first term may be regarded as expressing the effect of excess of unit positive charges on the phase β side of the interphase or

$$Q^{\beta} = Fm_{M^{(z+1)+,N}}^{\sigma} \quad (3.20)$$

so that when (3.19) is put back into Eq. (3.2) a form equivalent to (3.13) is obtained:

$$dU^{\sigma} = T dS^{\sigma} - p dV^{\sigma} + \gamma dA_s + \sum_{j=1}^{j=J^{\alpha}} \mu_{j,e}^{\alpha} dm_{j,e}^{\sigma} + \sum_{j=J_0+1}^{j=J_0-2} \sum_{k=0}^{k=K-1} \mu_{j,k}^{\beta} dm_{j,k}^{\sigma} + \varepsilon dQ^{\alpha} + \mu_{M^{(z+1)+,N}}^{\sigma} dm_{\Sigma M}^{\sigma} \quad (3.21)$$

the difference being that, here, two terms are lost from the sum for phase β and none from the sum for phase α instead of one from each.

The ideal polarized interface is a special case of the two types of non-polarizable discussed above. If it is assumed that in (3.13), $m_M^{\alpha} \rightarrow 0$, the possibility of charge transfer vanishes. This causes modifications in the last two terms of (3.13). At first sight it would appear from (3.11) that Q^{α} also vanishes; however, it must be noted that this quantity actually represents the excess of electrons on the phase α side of the interphase. This in fact does not vanish as $m_M^{\alpha} \rightarrow 0$, but becomes more precisely interpretable as a physical charge because there is no longer any ambiguity about the location of the M^{z+} ions, since they may all be attributed to the phase β side of the interphase. At the same time the last term of (3.13) expresses simply the effect of a change of the amount of MN on the phase side of the interphase.

Similar changes occur in (3.21) if the corresponding assumption is made, namely, that the concentration $m_{M^{(z+1)+,N}}^{\alpha} \rightarrow 0$. Again the possibility of charge transfer vanishes and again the interpretation of the last two terms is modified. Q^{α} remains finite and becomes clearly related to a physical charge on the β phase side of the interphase because it represents the excess of unit positive charges. At the same time $m_{\Sigma M}^{\sigma}$ reduces to $m_{M,N}^{\sigma}$. Consequently, both (3.13) and (3.21) lead to the basic result

$$dU^{\sigma} = T dS^{\sigma} - p dV^{\sigma} + \gamma dA_s + \varepsilon dQ^{\alpha} + \sum_{j=1}^{j=J_0-1} \sum_{k=0}^{k=K-1} \mu_{j,k} dm_{j,k}^{\sigma} \quad (3.22)$$

in which the concentration terms for both phases are regrouped together and the sum covers all but one of the neutral components of the two bulk phases. If one of the terms of this sum is given the interpretation of the last term of (3.13) or that of the last term of (3.21), then it is possible to use the form (3.22)