

Electrochemical Thermodynamics

3.1 Equilibrium Cell Potential and Gibbs Energy

As discussed in Chap. 2 any chemical reaction involving charge exchange between two different redox reactants, see Eqs. (3.1 a,b) can be performed virtually – and very often also practically – by performing the redox reactions of the two redox-couples separately at two different electrodes but jointly in a divided electrochemical cell (Fig. 3.1):



thus the oxidation of ferrous ions by ceric ions



may be performed in two half cells, one containing the ferric/ferrous system ($Fe^{2+} \rightarrow Fe^{3+} + e^{-}$), the other containing the ceric/cerous system ($Ce^{4+} + e^{-} \rightarrow Ce^{3+}$).

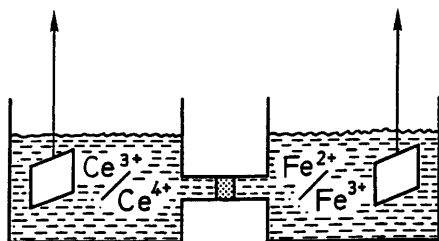


Fig. 3.1. Schematic of a cell reaction composed of two separate redox reactions which jointly would establish a homogeneous redox reaction between an oxidant and a reductant.

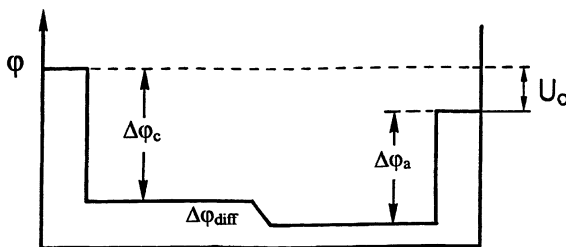


Fig. 3.2. Equilibrium cell potential U_0 in a cell divided by a diaphragm composed of two interfacial potentials $\Delta\phi_i$ and a (mostly negligible) diffusion potential $\Delta\phi_{diff}$. The diffusion potential $\Delta\phi_{diff}$ vanishes if a salt bridge with an electrolyte whose cations and anions possess transference numbers of 0.5, each, connects the two separate cells. With aqueous KCl solutions this is the case

Both being connected by a salt bridge¹⁾, they deliver an electrical potential difference U_0 between two Pt-electrodes inserted into the two separated electrolytes (Fig. 3.2)

Likewise the formation of hydrochloric acid, dissolved at a given concentration in water, from gaseous chlorine and gaseous hydrogen, realized in two half cells connected by an electrolyte bridge, generates a cell potential. If the reaction is performed electrochemically, ($H_2 + Cl_2 \rightleftharpoons 2HCl$; $H_2 \rightleftharpoons 2H^+ + 2e^-$ and $Cl_2 + 2e^- \rightleftharpoons 2Cl^-$), by dipping a chlorine electrode (made of platinized platinum and being supplied and sparged with elemental chlorine) and a hydrogen electrode (platinized, H_2 -sparged platinum electrode) into an aqueous solution of hydrochloric acid of the respective concentration, the equilibrium cell potential can be measured between the two platinum electrodes at vanishing current with a voltmeter of high internal resistance.

This cell potential is sometimes called “electromotive force”. Under conditions of vanishing cell current and established reversibility of the two different electrode reactions, (which is accomplished by effective electrocatalysis of the two electrode reactions by applying for instance platinum black), the so called open cell potential becomes the equilibrium cell voltage U_0 .

U_0 equals the free energy ΔG of the cell reaction per mol of product divided by the number ν_e of Faradays ($1F=96,500$ As) necessary for the electrochemical generation of one mol of product.



1 The connecting electrolyte in the bridge should have equal transference numbers (0.5) for cations and anions imposing equal distribution of cationic and anionic currents on the cell.

U_0 is defined as the equilibrium potential difference between the respective anode and cathode.

$$U_0 = E_0(\text{anode}) - E_0(\text{cathode}) \quad (3.2 \text{ d})$$

$$U_0 = \frac{\Delta G}{v_e F} \quad (3.3)$$

where $v_e = 1$ for HCl.

If the reaction Eq. (3.2 a) proceeds spontaneously, the hydrogen electrode is the anode and if the electronic current passes through a wire or a load from the anode to the cathode, then ΔG is negative and the cell would spontaneously produce hydrochloric acid. For HCl electrolysis, however, the chlorine electrode is the anode, the hydrogen electrode becomes the cathode, and under these conditions where reaction at Eq. (3.2 a) is reversed by imposing an external potential differentially greater than U_0 , hydrochloric acid would be electrolytically decomposed and ΔG becomes positive.

The Gibbs energy of any chemical reaction depends on:

- (1) the temperature;
- (2) the concentrations of dissolved reactants; and
- (3) the partial pressures of gaseous reactants.

Because of the latter two dependencies it is reasonable to define standard molar Gibbs energies called standard chemical potentials μ_i^0 and also standard cell voltages U^0 defined by standard concentrations and standard pressures of reactants and products. Standard concentrations of dissolved substances – in particular for aqueous solutions of electrolytes are defined by solute activities of 1 mol dm^{-3} and for gaseous substances by partial fugacities of 0.1 MPa or 1 bar respectively.

Concentration related activities and fugacities are derived from actual concentrations and partial pressures by multiplying molar concentrations with activity coefficients, γ_i ,

$$a_i = c_i \gamma_i \quad (3.4 \text{ a})$$

or partial pressures with fugacity coefficients f_i ,

$$p_i^* = p_i f_i. \quad (3.4 \text{ b})$$

These coefficients account for deviations from ideal behaviour which is described by the two limiting equations, Eqs. (3.5 a, b), which describe chemical potentials of gases and solutes at low – or more precisely – vanishing pressures and concentrations.

$$\mu_i = \mu_i^0 + RT \ln(p_i/p^0) \quad (3.5 \text{ a})$$

where p^0 is standard fugacity (0.1 MPa)

$$\mu_j = \mu_j^0 + RT \ln(c_j/c^0) \quad (3.5 \text{ b})$$

c^0 is standard activity (1 mol dm^{-3}), μ_i and μ_j are chemical potentials or molar free enthalpies of either gaseous species i or dissolved materials j .

Reduced quantities p_i/p^0 and c_j/c^0 , which are very often omitted in the literature and will be also omitted in the book from hereon, are used in order to make the argument of the logarithms adimensional.

The corrected equations for higher pressures and concentrations read

$$\mu_i = \mu_i^0 + RT \ln(p_i f_i) \quad (3.5 \text{ c})$$

$$\mu_j = \mu_j^0 + RT \ln(c_j \gamma_j) \quad (3.5 \text{ d})$$

Introducing Eqs. (3.5 c,d) into Eq. (3.3) and neglecting deviations from ideality yields

$$U_0 = \left\{ \sum v_{i,j} \mu_{i,j}^0 + RT \ln \left(\prod_{i,j} c_j^{v_j} p_i^{v_i} \right) \right\} / (v_e F) \quad (3.6)$$

with $v_{i,j}$ the stoichiometric factors of gaseous, index i , and dissolved, index j , reactants and products of the cell reaction; $v_{i,j}$ is positive for products and negative for educts and v_e is the stoichiometric factor of electrons for the reaction under consideration..

For the hydrogen/chlorine cell this translates into

$$FU_0 = \Delta G_{\text{HCl}}^0 + RT \ln \left\{ (p_{\text{H}_2} p_{\text{Cl}_2})^{1/2} c_{\text{HCl}}^{-1} / (\text{mol}^{-1} \text{dm}^3 \text{bar}) \right\} \quad (3.6 \text{ a})$$

Equation (3.6 a) defines the concentration and pressure dependence of the cell potential of the hydrochloric acid cell and simultaneously the so called standard equilibrium potential U^0 of the cell reaction

$$U_{\text{HCl}}^0 = \Delta G_{\text{HCl}}^0 / F \quad (3.6 \text{ b})$$

which is the equilibrium cell potential of a hypothetical cell in which all reactants and products possess standard activities and fugacities respectively.

ΔG^0 determines the equilibrium coefficient $K_{p,c}$ of the chemical reaction

$$\Delta G^0 = -RT \ln K_{p,c} \quad (3.6 \text{ c})$$

so that the measurement of equilibrium cell potentials combined with their extrapolation to standard condition is used to determine data for chemical equilibria, in particular for chemical equilibria which involve dissolved electrolytes.

For the chosen chlorine/hydrogen cell the corresponding relation, which allows to determine the standard Gibbs energy, reads

$$U_{\text{HCl}}^0 F = \Delta G_{\text{HCl}}^0 = -RT \ln K = -RT \ln \left[a_{\text{HCl, diss}} / (p_{\text{H}_2} \cdot p_{\text{Cl}_2})^{1/2} \right]_{\text{equil}} \quad (3.6 \text{ d})$$

For the electrochemical engineer it is most important to note that the equilibrium cell potential U_0 determines the minimum amount of electrical energy which has to be expended for any given electrochemical conversion or electrolysis process ($\Delta G > 0$) accounting for any given concentration and pressure of reactants and products or the maximal amount of electrical energy which can be generated from a battery or a fuel cell ($\Delta G < 0$) which is driven by the respective reaction. Any irreversibility in a practically performed electrochemical process increases the expended electrical energy for an energy consuming electrolysis and decreases the extractable electrical energy from a fuel cell or a battery.

3.2

Electrode Potentials, Reference Electrodes, Voltage Series, Redox Schemes

For vanishing cell currents and neglecting diffusion potentials the electrical potential in the electrolyte is constant between the two electrodes (Fig. 3.2). Therefore the equilibrium cell voltage U_0 is to a good approximation equal to the difference of the two so-called interfacial potentials $\Delta\phi_a$ and $\Delta\phi_c$ which exist at the phase boundaries anode/electrolyte and cathode/electrolyte. Interfacial potentials mean differences of internal potentials of neighboured phases:

$$U_0 = [\Delta\phi_a - \Delta\phi_c]_{i=0} = [(\phi_a - \phi_{el}) - (\phi_c - \phi_{el})]_{i=0} \quad (3.7)$$

For principle reasons the internal potential differences $\Delta\phi_a$ and $\Delta\phi_c$ which are called interfacial potentials cannot be measured whereas the difference of interfacial potentials occurring in electrochemical cells are well defined and easily measurable quantities. If one of these interfacial potentials is fixed by a rapidly established electrochemical equilibrium which does not vary with time, a change in $\Delta\phi_a - \Delta\phi_c$ reflects any change in the second non-fixed interfacial potential.

This is the reason to introduce reference electrodes which possess themselves well defined and easily reproducible, though principally unknown, interfacial potentials $\Delta\phi_{\text{reference}}$ (Fig. 3.3) in order to measure electrode potentials of single electrodes vs. such fixed electrode potential of the reference electrode. As the most popular example of a reference electrode we refer to the normal hydrogen or standard hydrogen electrode (NHE). This reference electrode, which is by no means a uniquely distinguished reference, is a hypothetical hydrogen electrode which dips into an acidic aqueous solution in which protons possess the activity (activity means activity coefficient corrected concentration) of 1 mol dm^{-3} and is sparged with hydrogen of 0.1 MPa pressure (more precisely with a fugacity of 0.1 MPa). Other practical reference electrodes are for instance the 0.01n HCl/hydrogen electrode, the KCl-saturated calomel electrode (SCE: Hg, covered by a $\text{Hg}_2\text{Cl}_2/\text{Hg}$ mixture and being in contact with a saturated aqueous potassium chloride solution) or 1 mol l^{-1} or also a KCl-saturated silver/silver chloride electrodes 1 mol l^{-1} KCl Ag/AgCl or KCl_{sat} Ag/AgCl which are connected electrolytically by means of an electrolyte bridge most often in the form of a Luggin - capillary, filled with aqueous saturated KCl-solution, Fig. 3.3, to the electrode under

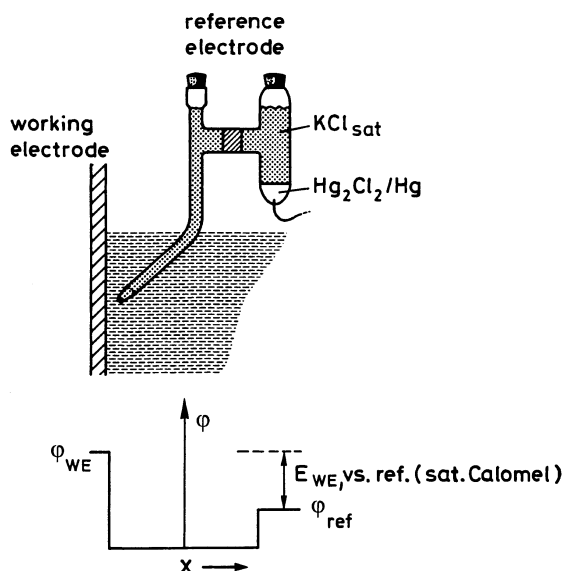


Fig. 3.3. Schematic description of the use of the interfacial potential $\Delta\phi_{ref}$ of a reference electrode in an electrochemical cell by means of an electrolyte bridge, most often filled by sat. KCl solution. The electrolyte bridge is introduced in the form of a so called Luggin-capillary. Index $_{WE}$ means working electrode

investigation. Of practical importance is the reversible hydrogen electrode (RHE) in any respective electrolyte solution which can very often be established by dipping a Pt-black activated Pt-electrode into the electrolyte and sparging it with pure hydrogen.

The RHE-potential is defined by the proton-activity of the solution under study and is – although well defined – not a solvent/solute independent quantity since it is determined by the pH of the electrolyte under consideration. The RHE is of high practical value in those electrochemical systems in which water is decomposed (water electrolysis) or formed (fuel cells). It is therefore often used as reference for any hydrogen or oxygen evolving electrode process and the respective hydrogen or oxygen consuming fuel-cell electrodes. Likewise useful is the reversible chlorine electrode for all systems where chlorine is evolved or electrochemically reduced. Table 3.1 collects some of the more popular reference electrodes used for measurements in aqueous solutions and their potential with respect to the standard or normal hydrogen electrode (vs. NHE).

The difference of the interfacial potential of any arbitrary electrode under study and that of any selected reference electrode is called the electrode potential versus the chosen reference-electrode. (For instance: +0.2 V vs KCl sat. calomel, or in abbreviated form: +0.2 V vs SCE).

Although the normal hydrogen electrode is by no way distinguished among all possible reference electrodes it had been distinguished historically and by convention as the preferred reference for all electrode-potential measurements in aqueous

Table 3.1. List of reference electrodes at 25 °C

Electrode	Potential/V
standard hydrogen (NHE)	0
reversible hydrogen (RHE)	$-0.059 \cdot \text{pH}$
calomel, KCl sat. (SCE)	+0.243
calomel, 1 mol l ⁻¹ KCl sat. (NCE)	+0.2828
silver/silver chloride, 1 mol l ⁻¹ KCl (NSE)	+0.2224
aqu. Quinhydrone	+0.699

solution and the (unknown) value of the internal potential difference of the standard hydrogen electrode, $\Delta\Phi_{\text{H}_2}^0$, is deliberately and per definitionem taken to be zero.

The standard potential value of any other equilibrium electrode (all participating reactants possess either unit activity, if they are pure phases or all concentration activities of dissolved reactants equal 1 mol/dm³ or gas fugacities equal 0.1 MPa or 1 bar respectively) are referred to the potential of the standard hydrogen electrode and correspondingly ordered in the voltage series.

The voltage series for aqueous solutions of a number of metal/metal ion electrodes of practical interest is collected in Table 3.2 a, for element/element-anions electrodes in Table 3.2 b and for redox couple electrodes, where the reduced as well as the oxidised species is dissolved in solution, in Table 3.2 c.

The concentration dependence of the equilibrium potential of a redox couple



is given by the Nernst equation

$$E = E^0 + \frac{RT}{F} \ln \frac{c_{\text{A}}}{c_{\text{A}^-}} \quad (3.8 \text{ b})$$

For the more involved and more generally formulated redox-reaction which is written with omission of the electric charge of species A and B



one obtains the Nernst equation

$$E = E^0 + \frac{RT}{v_{\text{e}}F} \ln \frac{c_{\text{A}}^{v_{\text{A}}}}{c_{\text{B}}^{v_{\text{B}}}} \quad (3.9 \text{ b})$$

Table 3.2 a. Normal potentials in Volt of selected cation-element couples¹⁾

Li/Li ⁺	-3.01	Se/Se ³⁺	-2.0	Ti/Ti ⁺	-0.335	Cu/Cu ²⁺	+0.34
Rb/Rb ⁺	-2.98	Ti/Ti ²⁺	-1.75	Co/Co ²⁺	-0.27	Os/Os ²⁺	+0.7
Cs/Cs ⁺	-2.92	Al/Al ³⁺	-1.66	Ni/Ni ²⁺	-0.23	Rh/Rh ³⁺	+0.7
K/K ⁺	-2.92	V/V ²⁺	-1.5	Sn/Sn ²⁺	-0.14	Tl/Tl ³⁺	+0.71
Ba/Ba ²⁺	-2.92	Nb/Nb ³⁺	-1.1	Pb/Pb ²⁺	-0.126	Hg ₂ /Hg ₂ ²⁺	+0.796
Sr/Sr ²⁺	-2.89	Mn/Mn ²⁺	-1.05	Fe/Fe ³⁺	-0.036	Ag/Ag ⁺	+0.799
Ca/Ca ²⁺	-2.84	Cr/Cr ²⁺	-0.86	H ₂ /2H ⁺	0.00	Pb/Pb ⁴⁺	+0.8
Na/Na ⁺	-2.713	Fe/Fe ²⁺	-0.44	Bi/Bi ³⁺	+0.2	Hg/Hg ²⁺	+0.854
La/La ³⁺	-2.4	Cd/Cd ²⁺	-0.44	Sb/Sb ³⁺	+0.24	Pt/Pt ²⁺	+1.2
Mg/Mg ²⁺	-2.38	In/In ³⁺	-0.34	As/As ³⁺	+0.3	Au/Au ³⁺	+1.42

Table 3.2 b. Normal potentials in Volt of some selected anion-element couples¹⁾

Te ²⁻ /Te	-0.92	2I ⁻ /I _{2 s}	+0.536	2Br ⁻ /Br _{2 g}	+1.08	2Cl ⁻ /Cl _{2 diss}	+1.40
Se ²⁻ /Se	-0.78	2I ⁻ /I _{2 diss}	+0.62	2Br ⁻ /Br _{2 diss}	+1.09	OH ⁻ /OH	+1.4
S ²⁻ /S	-0.51	2CNS ⁻ /(CNS) ₂	+0.77	ClO ₂ ⁻ /ClO _{2 g}	+1.15	2F ⁻ /F _{2 g}	+2.85
4OH ⁻ /O ₂ +H ₂ O	-0.401	2Br ⁻ /Br _{2 diss}	+1.066	2Cl ⁻ /Cl _{2(g)}	+1.358		

Table 3.2 c. Normal potentials in Volt of redox couples with soluble partners¹⁾

[Co(CN) ₆] ⁴⁻ / [Co(CN) ₆] ³⁻	-0.83	[Mn(CN) ₆] ⁴⁻ / [Mn(CN) ₆] ³⁻	-0.22	Hg ₂ ²⁺ /2Hg ²⁺	+0.906		
Ga ²⁺ /Ga ³⁺	-0.65	[Co(NH ₃) ₆] ²⁺ / [Co(NH ₃) ₆] ³⁺	+0.1	IrCl ₆ ³⁻ /IrCl ₆ ²⁻	+1.02		
In ²⁺ /In ³⁺	-0.45	Sn ²⁺ /Sn ⁴⁺	+0.15	3Br ⁻ /Br ₃ ⁻	+1.05		
Eu ²⁺ /Eu ³⁺	-0.43	Cu ⁺ /Cu ²⁺	+0.159	Ti ⁺ /Ti ³⁺	+1.28		
Cr ²⁺ /Cr ³⁺	-0.41	[Fe(CN) ₆] ⁴⁻ / [Fe(CN) ₆] ³⁻	+0.36	Au ⁺ /Au ³⁺	+1.29		
WCl ₅ ²⁻ /WCl ₅ ⁻	-0.4	3I ⁻ /I ₃ ⁻	+0.535	Ce ³⁺ /Ce ⁴⁺ (in 0.1 M H ₂ SO ₄)	+1.44		
Ti ²⁺ /Ti ³⁺	-0.37	MnO ₄ ²⁻ /MnO ₄ ⁻	+0.54	Mn ²⁺ /Mn ³⁺	+1.51		
In ⁺ /In ²⁺	-0.35	Fe ²⁺ /Fe ³⁺	+0.783	Pb ²⁺ /Pb ⁴⁺	+1.69		
V ²⁺ /V ³⁺	-0.255	OsCl ₆ ³⁻ /OsCl ₆ ²⁻	+0.85	Co ²⁺ /Co ³⁺	+1.842		

Table 3.2 d. Normal potentials in Volt of oxoanions and metal oxides¹⁾

Cr(OH) _{3s} /CrO ₄ ²⁻	-0.12	IO ⁻ /H ₃ IO ₆ ²⁻ , OH ⁻	+0.7	Mn ²⁺ /MnO ₄ ⁻ , H ⁺	+1.51
(PbO) _s /(PbO ₂) _s , OH ⁻	+0.248	VO ²⁺ /HVO ₃ , H ⁺	+1.1	Cl ⁻ /HClO ₂ , H ⁺	+1.56
(PbO) _s /(Pb ₃ O ₄) _s , OH ⁻	+0.25	Cr ³⁺ /Cr ₂ O ₇ , H ⁺	+1.33	MnO ₂ /MnO ₄ ⁻ , H ⁺	+1.7
TeO ₃ ²⁻ /TeO ₄ ²⁻ , OH ⁻	+0.4	Cl ₂ /ClO ₄ ⁻ , H ⁺	+1.34	Fe ³⁺ /FeO ₄ ²⁻ , H ⁺	+1.9
ClO ⁻ /ClO ₂ ⁻ , OH ⁻	+0.66	Cl ⁻ /HClO, H ⁺	+1.49	SO ₄ ²⁻ /S ₂ O ₈ ²⁻ , H ⁺	+2.01

¹⁾ Extracted from Dobos [1]

For a metal/metal ion electrode where the redox reaction at Eq. (3.10 a) is potential determining, and the metal of the electrodes is the pure material of activity 1



the Nernst equation reads

$$E = E_{M^{z+}/M}^0 + \frac{RT}{zF} \ln a_{M^{z+}} \quad (3.10 \text{ b})$$

or if activity corrections may be neglected ($a_{M^{z+}} = c_{M^{z+}}$) one obtains

$$E = E_{M^{z+}/M}^0 + \frac{RT}{zF} \ln c_{M^{z+}} \quad (3.10 \text{ c})$$

For an element/element-anion electrode as the chlorine electrode with gaseous chlorine

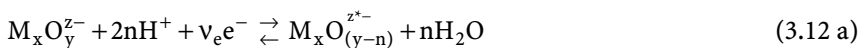


one obtains with neglect of activity coefficients

$$E = E_{X_2/X^{-}}^0 + \frac{RT}{F} \ln p_{X_2}^{1/2} / c_{X^{-}} \quad (3.11 \text{ b})$$

where in the second term of Eq. (3.11 b) ($a_{X_2} = f c_{X_2}$) is to be inserted instead of p_{X_2} if the molecular species X_2 , for instance bromine, is not supplied as a gas but is dissolved with the concentration c_{X_2} in the electrolyte.

A redox couple which may involve in its redox-reaction additionally the solvent, water, like for instance with the formation of metal oxo-anions from lower valent metal cations as with the couple chromate/chromium III or permanganate/Mn II or in general terms the reaction at Eq. (3.12 a):



with $z^* = z + v_e - 2n$, imposes onto an inert indicator electrode like a Pt wire an electrode potential which is pH-dependent:

$$E = E_{M_x O_y^{z-}/M_x O_{y-n}^{z*-}}^0 + \frac{RT}{v_e F} \ln \frac{c_{M_x O_y^{z-}} \cdot c_{H^{+}}^{2n}}{c_{M_x O_{y-n}^{z*-}}} \quad (3.12 \text{ b})$$

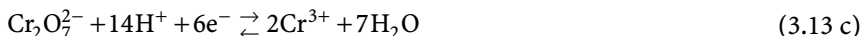
As an example chromate and chromic ions form a redox couple:



the electrode potential of which changes with $c_{\text{Cr}^{3+}}$, $c_{\text{CrO}_4^{2-}}$ and pH according to

$$\begin{aligned} E &= E^0_{\text{CrO}_4^{2-}/\text{Cr}^{3+}} + \frac{RT}{3F} \ln \frac{c_{\text{CrO}_4^{2-}} \cdot c_{\text{H}^+}^8}{c_{\text{Cr}^{3+}}} \\ &= E^0_{\text{CrO}_4^{2-}/\text{Cr}^{3+}} + \frac{RT}{3F} \ln \frac{c_{\text{CrO}_4^{2-}}}{c_{\text{Cr}^{3+}}} - \frac{RT}{3F} 2.302 \cdot 8 \cdot \text{pH} \end{aligned} \quad (3.13 \text{ b})$$

In acidic solutions bichromate instead of chromate is reduced



and the Nernst equation reads

$$E = E^0_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} + \frac{RT}{6F} \ln \frac{c_{\text{Cr}_2\text{O}_7^{2-}}}{c_{\text{Cr}^{3+}}^2} - \frac{RT}{3F} 2.302 \cdot 14 \cdot \text{pH} \quad (3.13 \text{ d})$$

Table 3.2 c lists some more prominent examples of this type of redox couples. Normal potentials refer in these cases to $a_{\text{H}^+}=1 \text{ mol dm}^{-3}$, that means to a pH of 0 or if hydroxyl ions are involved in the reaction to $a_{\text{OH}^-} = 1 \text{ mol dm}^{-3}$ or $\text{pH} = 14$ respectively.

The equilibrium cell potential for any process conditions may be obtained by calculating the difference of the two involved single electrode potentials. For this purpose starting from the normal potentials of Tables 3.2 a–d, single equilibrium electrode potentials are calculated by inserting concentrations (activities) and pressures (fugacities) of dissolved or gaseous reactants as they prevail under practical operating conditions into the respective Nernst equation.

In the membrane chloroalkali electrolysis, for instance, hydrogen (1 bar) is evolved at the cathode from a 30 wt% KOH solution, whereas the chlorine anode evolves chlorine (1 bar) from brine which contains approximately 200 g dm^{-3} NaCl (3.4 mol dm^{-3}). Omitting in a first approach any activity and fugacity corrections and calculating c_{NaOH} with $\rho_{30 \text{ wt\% NaOH}}=1.3 \text{ g cm}^{-3}$ to be $c_{\text{NaOH}}=6 \text{ mol dm}^{-3}$ one obtains for the single electrode potentials

$$E_{\text{Cl}_2} = E^0_{\text{Cl}_2} - (RT/F) \ln c_{\text{Cl}^-} = (1.40 - 0.032) \text{ V} = +1.368 \text{ V} \quad (3 \text{ a})$$

$$E_{\text{H}_2} = E^0_{\text{H}_2} - 2.302 \cdot RT/F \cdot \text{pH} = (0 - 0.887) \text{ V} = -0.887 \text{ V} \quad (3 \text{ b})$$

With this approximations one obtains:

$$U_0 (\text{chloroalkali electrolysis}) \approx (1.358 + 0.887) \text{ V} = 2.255 \text{ V} \quad (3 \text{ c})$$

This comes already quite close to the value of 2.3 V which is obtained by taking into account activity corrections – in particular for the concentrated caustic

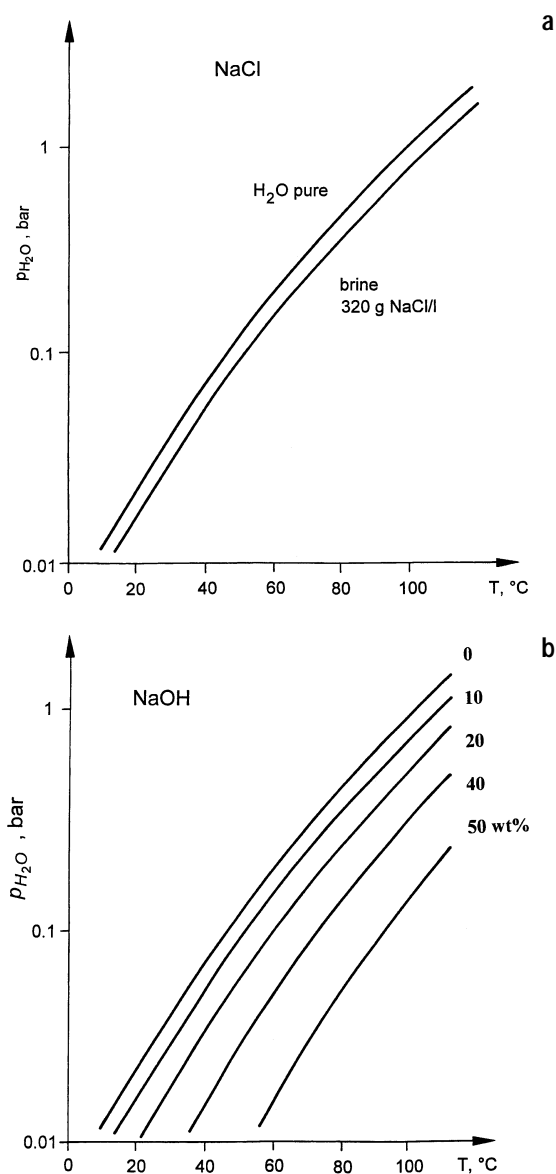


Fig. 3.4a,b. Temperature dependence of water vapour pressures of: a NaCl-solutions; b NaOH-solutions at various concentrations

soda solution of the catholyte. For technical electrolysis processes which often use highly concentrated electrolyte solutions, it is important to take into account that the activity of the solvent, which usually is water, cannot be assumed to be unity, but is very often considerably decreased.

As an example for decreased water activities in concentrated electrolytes, Fig. (3.4 a,b) plots the vapour pressures of pure water, of NaCl-solutions and of NaOH solutions of different concentrations vs temperature. The activity of the solvent at any temperature and any electrolyte concentration is calculated according to Eq. (3.14) from the ratio of the vapour pressures of the concentrated solution, p^c , and pure water p^0 .

$$a_{\text{H}_2\text{O}}^c = p_{\text{H}_2\text{O}}^c / p_{\text{H}_2\text{O}}^0 \quad (3.14)$$

Obviously the decrease of water activity with increasing electrolyte concentrations is higher for NaOH solutions than for NaCl solutions due to pronounced exergetic solute-solvent interaction

3.3

Reaction Enthalpy, Reaction Entropy, Thermoneutral Cell Voltage and Heat Balances of Electrochemical Reactions

Equation (3.3) defines the Gibbs free energy ΔG of any cell reaction as the minimal amount of electrical energy per mol of converted substrate which must be expended in an electrolysis process. This equation differs from the total energy balance and the heat balance of a given cell reaction which is performed under equilibrium conditions. The total energy to be converted is the reaction enthalpy ΔH which differs from ΔG by the entropic term $T\Delta S$

$$\Delta G = \Delta H - T\Delta S \quad (3.15)$$

For any electrolysis process ($\Delta G > 0$) which involves a positive reaction entropy, ΔG is smaller than ΔH and the entropic term $T\Delta S$ has to be supplied by introducing thermal heat from the environment into the cell, if the reaction is performed reversibly, but at constant temperature.

$$T\Delta S = \Delta H - \Delta G \quad (3.16)$$

If ΔS is negative, $T\Delta S$ must be transferred as heat from the cell to the environment.

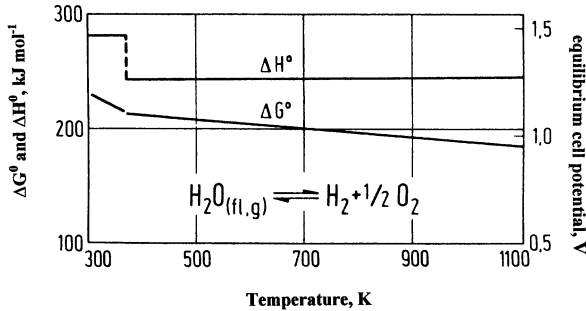
In general all electrolysis processes which involve gas evolution from a liquid electrolyte have a positive reaction entropy of the order of magnitude of R per mol of evolved gas.

Table (3.3 a) collects for four important electrolysis processes which involve gas evolution standard Gibbs enthalpies and reaction enthalpies together with standard entropies at the given process temperatures.

Figure 3.5 depicts the temperature dependence of ΔG^0 and ΔH^0 with the difference representing $T\Delta S^0$ of the most important water splitting/water formation reaction. For water formation ΔG^0 and ΔH^0 are negative for the formation of water. At 373 K the transition from liquid water to water vapour causes a drop in ΔH due to the heat of evaporation. Whereas ΔH^0 is almost constant from 373–1100 K, ΔG^0 decreases by approximately 20%. Only the quantity ΔG^0 can be con-

Table 3.3. a Thermodynamic data. **b** Equilibrium voltage, U_0 , and thermoneutral cell voltage U_{th} of some cell reactions with gas evolution

Cell reaction		(a)			(b)	
		$\Delta G^0/\text{kJmol}^{-1}$	$\Delta H^0/\text{kJ mol}^{-1}$	$\Delta S^0/\text{Jmol}^{-1}\text{K}^{-1}$	U_0/V	U_{th}/V
$(\text{H}_2\text{O})_l \rightarrow \text{H}_2 + 1/2\text{O}_2$	100 °C	224	277.5	+159	1.16	1.42
$(\text{H}_2\text{O})_g \rightarrow \text{H}_2 + 1/2\text{O}_2$	100 °C	224	243	+50	1.16	1.25
$(\text{Al}_2\text{O}_3)_s \rightarrow 2\text{Al}_l + 3/2\text{O}_2$	1300 K	1263	1688	+326	2.18	2.9
$2(\text{Al}_2\text{O}_3)_{\text{diss}} + 3\text{C}_s \rightarrow 3\text{CO}_2 + 4\text{Al}$	1300 K	1763	2189	+431	1.89	1.89

Fig. 3.5. ΔG^0 , ΔH^0 and U_0 of the water splitting/water formation reaction from 300 to 1100 K

verted into electricity in a fuel cell and must at least be expended in water electrolysis.

Whenever the electrolysis process has to be assumed to be performed under adiabatic conditions, which is almost realised in large industrial electrolyzers, the total reaction enthalpy must be provided for by expending electrical energy so that instead of U_0 – the minimal or equilibrium cell voltage – the so called “thermoneutral” cell voltage U_{th} or ΔH cell voltage must be applied in order to balance the input of electrical energy with the enthalpy demand of the cell reaction.

$$U_{th} = \Delta H / (v_e F) \quad (3.17)$$

In order to perform the electrolysis process under adiabatic conditions without temperature change of the electrolyte U_{th} has to be the steady state cell voltage. Table 3.3 b compares equilibrium cell voltages U_0 and “thermoneutral” U_{th} cell voltages of the electrolysis processes which are listed in Table (3.3) under (a).

3.4 Heat Balances of Electrochemical Processes

Under technical conditions electrolysis processes are always performed irreversibly so that actual cell voltages exceed the equilibrium cell voltages often by far.

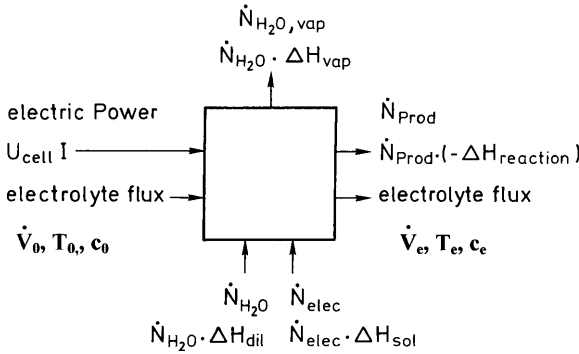


Fig. 3.6. Balance of electric power-input, electrochemical energy demand and generated heat

For a fuel cell process the fuel cell voltage is correspondingly lower than U_0 . The heat Q generated in excess per mol of product is calculated by

$$Q_{\text{molar}} = U_{\text{cell}} \nu_e F - \Delta H \quad (3.18)$$

Since most technical electrolysis processes are performed at elevated temperatures, that means in the temperature range between 70 and 90 °C, the evolved gases which, being by the very nature of their generation fully saturated with water vapour, carry away substantial amounts of heat by the respective amount of latent heat of vaporisation which is eventually removed from the product gas stream in coolers by condensing of the water vapour.

In chloroalkali electrolysis according to the membrane process the catholyte is 30 wt% NaOH and the anolyte is brine with 200 g NaCl dm⁻³. At a process temperature of 90 °C, the chlorine gas leaving the cell contains approximately 60 mol% of water vapour whereas the evolved hydrogen – due to the diminished water activity in 30 wt% NaOH solutions – contains approximately only 30 mol% of H₂O. Per mol of H₂ or Cl₂ evolved, approximately 0.9 mol of water evaporate in total, which with a molar heat of evaporation of 38 kJ mol⁻¹ are able to remove approximately 34 kJ mol⁻¹ of chlorine from the cell or per two mol of NaCl converted in the process.

The total energy balance of an operating cell (Fig. 3.6) comprises the following terms per unit time:

- (i) the reaction enthalpy:

$$\dot{n}_p \Delta H_r$$

- (ii) convective heat transport due to heating of the circulating electrolyte:

$$\dot{V}_{\text{el}} \rho c_p (T_{\text{out}} - T_{\text{in}})$$

- (iii) heat removal by solvent evaporation:

$$\dot{N}_{\text{H}_2\text{O},\text{vap}} \cdot \Delta H_{\text{vap}} = I \sum_j \frac{1}{v_{e,j} F} \left(\frac{P_{\text{H}_2\text{O}}}{P - P_{\text{H}_2\text{O}}} \right) \cdot \Delta H_{\text{vap}}$$

- (iv) enthalpies of dissolution or dilution for those cases where pure solvent or solid or concentrated electrolyte is fed directly into the cell additionally to the recirculated electrolyte:

$$\dot{N}_{\text{salt}} \Delta H_{\text{diss}} + \dot{N}_{\text{H}_2\text{O}} \cdot \Delta H_{\text{dil}}$$

- (v) consumed electrical energy

$$U_{\text{cell}} I$$

$\dot{N}_{\text{H}_2\text{O}}$ and \dot{N}_{salt} are the molar fluxes of pure water and salt or other electrolytes per unit time which might be added continuously to the cell additionally to the volumetric flow rate \dot{v} of the electrolyte solution, which enters and leaves the cell under steady state conditions.

Equation (3.19) adds these different terms and equates them to the dissipated electric power

$$(vi) \quad U_{\text{cell}} I = (\Delta H_r / v_e F) I + \dot{V}_{\text{el}} \rho c_p (T_{\text{out}} - T_{\text{in}}) + \dot{N}_{\text{salt}} \cdot \Delta H_{\text{diss}} + \dot{N}_{\text{H}_2\text{O}} \cdot \Delta H_{\text{dil}} + I \sum_j \frac{1}{v_{e,j} F} \left(\frac{P_{\text{H}_2\text{O}}}{P - P_{\text{H}_2\text{O}}} \right) \cdot \Delta H_{\text{vap}} \quad (3.19)$$

In Eq. (3.19) all ΔH values are molar quantities (kJ/mol^{-1}) whereas the c_p -values of the circulated electrolyte is meant to be a mass specific quantity ($\text{kJkg}^{-1}\text{k}^{-1}$), hence multiplication of \dot{v} with density and specific heat c_p of the circulating electrolyte.

3.5

Retrieval of Thermodynamic Data and Activity Coefficients

Standard Gibbs free energies, enthalpies and entropies are collected for numerous compounds in JANAF Tables²⁾ and in other collections of thermodynamic data of, for instance, Baring and Knacke³⁾. Both explicitly mentioned data collections and others are not consistent with each other insofar as they choose different reference states.

2) JANAF tables are setting the standard Gibbs energies, enthalpies and entropies of all elements in their respective thermodynamically stable modification at any given temperature to zero. [2]

3) Baring and Knacke are setting Gibbs energies and enthalpies of all elements at the reference temperature of 298 K to zero whereas entropies are calculated for the elements from the third law [3]

Since most tables are referring only to pure elements or compounds respectively, concentration or pressure corrections to calculate free enthalpies under any condition of concentration and pressure must be applied. Neglecting to a first approximation activity (fugacity) coefficients one obtains for gases:

$$\mu_i(\text{gas}) = \mu_i^0 + RT \ln p_i \quad (3.20 \text{ a})$$

for solutions of non-ionised compounds

$$\mu_j(\text{solute}) = \mu_j^0 + RT \ln c_j \quad (3.20 \text{ b})$$

and for ideal solid solutions and liquid mixtures of non-ionised components with mol fractions extending from zero to unity, where the standard state is the pure substance

$$\mu_k(\text{mixture}) = \mu_k^0 + RT \ln x_k \quad (3.20 \text{ c})$$

with x_k being the mole fraction of the k_{th} component. Regard that μ_j^0 and μ_k^0 are not identical as they refer to different concentration scales and reference states. Since only the logarithm of activity and fugacity coefficients enter into the calculation of more refined data of free enthalpies, the approximate equations which neglect the deviation from ideal behaviour are very often of sufficient accuracy. For solutions of ionised compounds the situation is more complex because usually solute/solvent and solute/solute (interionic) interaction are non-negligible.

Molten mixtures of salts (for instance mixed NaCl/KCl melts), however, as far as they do not exhibit miscibility gaps can often be assumed to behave as almost ideal mixtures according to Eq. (3.20 c). For more refined calculations the empirical approximation given in Eq. (3.20 d) is used for the solvent or host melt, index 1, and for the solute, index 2. α and I are adjusted parameters.

$$\lg \gamma_1 = \alpha x_2 \quad (3.20 \text{ d})$$

$$\lg \gamma_2 = \alpha x_1^2 + I \quad (3 \text{ e})$$

This approximation holds for $0.5 < x_1 < 1$.

Often there exists a strong chemical interaction between the two components of a binary salt mixture or salt melt as for instance between alkali chlorides (LiCl, NaCl or KCl) and aluminium chloride due to complex formation



These binary mixtures can be described to a good approximation as an ideal binary mixture of the two species MCl and MAlCl₄ as far as the molar ratio of aluminium chloride to alkali chloride is kept below 1.

For dilute aqueous solutions of strong electrolytes composed of two monovalent ions, for instance HCl, the concentration of which do not exceed 10^{-2} mol

dm^{-3} the approximation of Debye and Hückel for single ion activity coefficients γ_{\pm} reads

$$\lg \gamma_{\pm} = A I^{1/2}; \quad I = \text{ionic strength} = 1/2 \sum c_i z_i^2 \quad (3.22)$$

with c the molar concentration of the ions, and the numerical value of A given by

$$\ln A = \frac{c e_0^2}{2.303 \cdot 2 \cdot \epsilon \cdot \epsilon_0 RT} \quad (3.22 \text{ a})$$

e_0 is the elemental charge, and ϵ, ϵ_0 the dielectric constant and induction coefficient and c the molar concentration of a 1:1 electrolyte.

Equation (3.22) allows one to calculate activity coefficients of single ions and mean activity coefficients of the dissolved electrolytes for relatively diluted electrolytes $\gamma_{\pm} = \{(\gamma_+) \cdot (\gamma_-)\}^{1/2}$ for 1:1 electrolytes, and in general

$$\gamma_{\pm} = \left\{ (\gamma_-)^{z^+} \cdot (\gamma_+)^{z^-} \right\}^{\frac{1}{z^+ + |z^-|}}.$$

But this equation fails at concentrations higher than 10^{-2} molar concentrations and is therefore only of limited value for electrochemical engineers who usually deal with concentrated electrolyte solution.

Since the electrochemical engineer has in most cases to apply his calculations to electrolyte concentrations from 1 mol dm^{-3} upwards where these simplified approximations based on calculations of the coulombic ion/ion interaction under complete neglect of solute/solvent interactions fail, he has to account for activity corrections mainly by evaluating empirical data. For those higher electrolyte concentrations it is meaningless to aim at calculating single ion activities and the experimental determination of total activities and activity coefficients of dissolved electrolytes should be performed instead. Nearly any method applied for the investigation of thermodynamic properties of higher electrolyte concentration like for instance ebullioscopy, cryoscopy, osmometry or vapour pressure determination determines solvent activities rather than solute activities and calculates solute activities by integrating the Gibbs–Duhem equation for isothermal mixing under constant pressure

$$N_i d\mu_i = 0 \quad (3.23)$$

which results in

$$\lg \gamma_{el} = \int_1^{x_{\text{solv}}} \frac{x_{\text{solv}}}{1 - x_{\text{solv}}} d \ln \gamma_{\text{solv}} \quad (3.24)$$

x_{solv} is the mole fraction of the solvent and γ_{solv} is its activity coefficient which can be measured relatively easily.

Figure 3.4 a,b is an example for the determination of water vapour pressures of concentrated electrolyte solutions which allow to determine the activity and activity coefficients respectively of water in these solutions by making use, for instance, of Eq. (3.14). Solving Eq. (3.24) by measuring γ_{solv} over an extended concentration range of the electrolyte. This meets the difficulty that for low electrolyte concentrations ($x_{\text{solv}} \rightarrow 1, (1-x_{\text{solv}}) \rightarrow 0$) the solvent activity approaches 1, $\log \gamma_{\text{solv}}$ approaches zero and $x_{\text{solv}}/(1-x_{\text{solv}})$ approaches ∞ so that the integral cannot be evaluated.

Using the Gibbs Duhem equation (Eq. 3.23) in the form

$$n_{\text{solv}} d \ln a_{\text{solv}} = n_{\text{elyte}} d \ln a_{\text{elyte}} \quad (3.23 \text{ a})$$

multiplying both sides of the equation with $1000/M_{\text{solv}}n_{\text{solv}}$, applying concentration definition on the molality scale, c_m and making use of the osmotic coefficient, f_{osm} , which is easily measured e.g. by cyroscopy and defines the solvent activity at low electrolyte concentration one arrives at Eq. (3.25) [4]:

$$\ln \gamma_{\pm} = (f_{\text{osm}} - 1) + 2 \int_0^c \frac{f_{\text{osm}} - 1}{c_m^{1/2}} d c_m^{1/2} \quad (3.25)$$

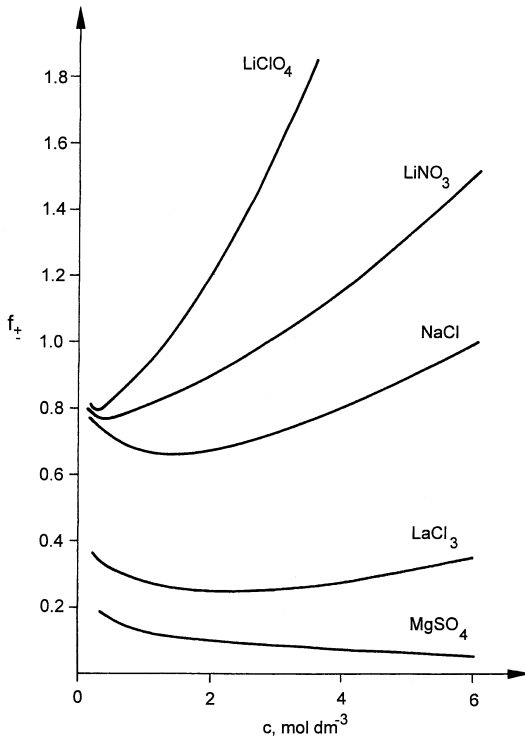


Fig. 3.7. Concentration dependence of electrolyte activity coefficients in concentrated solutions of various electrolytes

which can be integrated as the quantity $(f_{\text{osm}} - 1) / c_m^{1/2}$ converges towards a finite value as $c_m^{1/2}$ approaches zero. The mean ion activity coefficient γ_{\pm} is defined by Eq. (3.26):

$$(\gamma_{\pm})^{z_i + |z_j|} = (\gamma_{i,+})^{z_i} (\gamma_{j,-})^{|z_j|} \quad (3.26)$$

Figure 3.7 shows for several electrolytes the dependence of experimentally determined activity coefficients vs electrolyte concentration for aqueous solutions at ambient temperature. Typically activity coefficients of dissolved electrolytes which are composed of higher valent ions – in particular cations – at first decrease steeply with increasing concentration, pass through a minimum and then increase again – very often surmounting unity at higher concentrations.

A host of activity coefficient measurements for concentrated electrolytes is found in the scientific literature. They have been collected critically by Dobos [1] in 1975.

3.6 Thermodynamics of Electrosorption

The electrosorption of reaction educts, products or reaction intermediates that means their adsorption on the electrode surface does not bear on the thermodynamics of an electrochemical process because electrosorption is always an intermediate step of the overall reaction. But electrosorption is important for electrode processes and electrocatalysis and their kinetics. Very often electrochemical reactions demand adsorption of the educt or some reaction intermediate prior to the decisive, rate determining charge transfer. Therefore as an appendix to “Electrochemical Thermodynamics” the thermodynamics of electrosorption is treated in this chapter in a general way.

The thermodynamics of electrosorption of charged particles differ fundamentally from that of uncharged particles in so far as for charged particles the Gibbs energy of adsorption ΔG_{ad} is directly influenced by the interfacial potential difference at the phase boundary or the electrode potential respectively – compare Eq. (3.29) below. For uncharged particles the electrode potential influences the free energy of adsorption more indirectly, as the difference between the actual electrode potential and the respective potential of zero charge E_{pzc} the so called rational potential, $E_r = E - E_{\text{pzc}}$, determines the magnitude of ΔG_{ad} of uncharged particles. ΔG_{ad} for uncharged particles frequently changes with the rational potential according to $(E - E_{\text{pzc}})^{-2}$. For charged particles one cannot distinguish “true adsorption” that means incorporation of the species under consideration into the inner Helmholtz layer from accumulation in the diffuse part of the double layer, where at least two sheets of solvent molecules separate the respective charged particle from the electrode surface. Uncharged particles are not subject to this type of accumulation in the diffuse layer. The formal thermodynamic description of electrosorptive processes as well as that of simple ad-

sorption also has to take into account that the free energy of adsorption usually is influenced by the mutual interaction of the adsorbed particles, that means that the degree of coverage in contrast to the simple model of the Langmuir isotherm generally alters the adsorption enthalpy.

The Frumkin model postulates a linear dependence of the adsorption enthalpy ΔH_{ad} on the degree of coverage, Θ

$$\Delta H_{\text{ad}} = \Delta H_{\text{ad}}^0 + \beta \Theta \quad (3.27)$$

For charged as well as for uncharged particles “true” electrosorption in the meaning of contact-adsorption or adsorption in the inner and/or outer Helmholtz layer is often described by the generalised formula (Langmuir isotherm) which holds too for adsorption on solid surface from the gas phase.

$$\Theta = \frac{Kc}{1+Kc} \quad \text{with} \quad \Delta G_{\text{ad}} = -RT \ln K \quad (3.28)$$

K is the adsorption equilibrium coefficient which depends on the electrode potential E and the coverage; c is the concentration of the adsorbate in the bulk of the electrolyte.

Correspondingly one obtains Eq. (3.29 a) for the adsorption equilibrium coefficient for charged particles:

$$K_{\text{charged}} = K_0 \exp \left\{ -\frac{\Delta \mu_{\text{ad}}^0 - zF\eta}{RT} \right\} \quad (3.29 \text{ a})$$

For charged particles with charge ze and Frumkin dependence of ΔH_{ad} this equilibrium constant reads

$$K_{\text{charged}} = K_0 \exp \left\{ -\frac{\Delta \mu_{\text{ad}}^0 - \beta \Theta - zF\eta}{RT} \right\} \quad (3.29 \text{ b})$$

For uncharged particles the last term vanishes whereas $\Delta \mu_{\text{ad}}^0$ very often contains implicitly the interfacial potential as $\Delta \mu_{\text{ad}}^0$ depends on the rational potential $E_r = (E - E_{\text{pzc}})$. The standard free enthalpy of adsorption $\Delta \mu_{\text{ad}}^0$ of uncharged species is often found to vary according to Eq. (3.30):

$$\mu_{\text{ad,uncharged}}^0 = \frac{A}{(E - E_{\text{pzc}})^2} \quad (3.30)$$

So for uncharged particles frequently the Gibbs adsorption enthalpy decreases strongly with increasing and decreasing electrode potential starting from the point of zero charge.

Therefore it is a rule that uncharged particles are adsorbed most strongly at the potential of zero charge and its vicinity, whereas anion adsorption increases with positive and cation adsorption with negative rational potential.

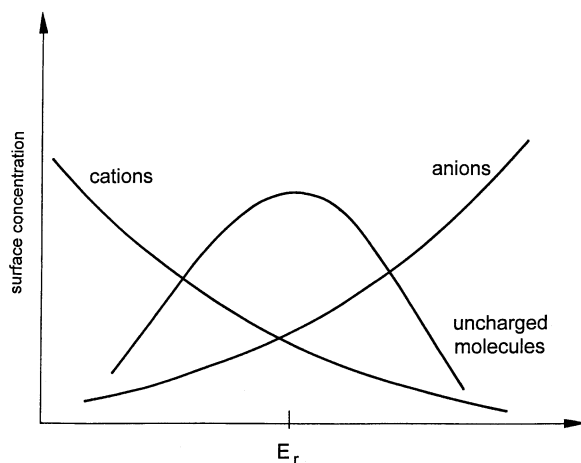


Fig. 3.8. Schematic representation of the dependence of surface concentrations on rational potential of anions, cations and uncharged molecules

Figure 3.8 depicts schematically the dependence of the surface concentration on the rational potential for different dissolved species. For non-surface-active ions the “surface concentrations” which means surface related excess in moles cm^{-2} and which must not be misunderstood as concentration of contact-adsorbed species vanish at potentials which are significantly more negative (anions) or positive (cations) than the point of zero charge and increase to very high virtually infinite values at potentials which deviate significantly in opposite direction because these ions are pushed out or attracted into the diffuse double layer by coulombic interaction with the electrode charge depending on the sign of the surface charge and the ion respectively. Surface active ions or neutral species, however, have easiest access to the Helmholtz layer at potentials close to the potential of zero charge where the Coulomb-interaction between the dipolar solvent molecules and the electrode charge vanishes as the charge vanishes. The solvent-electrode interaction increases strongly as the electrode charge increases with increasing deviation from the point of zero charge, that means with increasing positive or negative rational potential. Therefore at higher anodic or cathodic rational potentials surfactive bulky molecules are pushed out of the Helmholtz layer and replaced by solvent molecules.

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