1.3.10 Electrochemistry

Name	*Symbol*	*Definition*	*SI unit*	*Notes*
elementary charge, (proton charge)	e		C	
Faraday constant	F	$F = eL$	C mol^{-1}	
charge number of an ion	z	$z_B = Q_B/e$	1	(1)
ionic strength				
molality basis	I_m, I	$I_m = \frac{1}{2}\Sigma m_i z_i^2$	mol kg^{-1}	
concentration basis	I_c, I	$I_c = \frac{1}{2}\Sigma c_i z_i^2$	mol m^{-3}	(2)
mean ionic activity	$a_\pm$	$a_\pm = m_\pm \gamma_\pm / m$	1	(3),(4)
activity of an electrolyte	$a(A_{v+}, B_{v-})$	$a(A_{v+}, B_{v-}) = a_\pm^{(v_+ + v_-)}$	1	(3)
mean ionic molality	$m_\pm$	$m_\pm^{(v_+ + v_-)} = m_+^{v_+} m_-^{v_-}$	mol kg^{-1}	(3)
mean ionic activity coefficient	$\gamma_\pm$	$\gamma_\pm^{(v_+ + v_-)} = \gamma_+^{v_+} \gamma_-^{v_-}$	1	(3)

(1) The definition applies to entities B.

(2) To avoid confusion with the cathodic current, symbol I_c (note roman subscript), the symbol I or sometimes μ (when the current is denoted by I) is used for ionic strength based on concentration.

(3) v_+ and v_- are the numbers of cations and anions per formula unit of an electrolyte A_{v+}, B_{v-} .

Example For $Al_2(SO_4)_3$, $v_+ = 2$ and $v_- = 3$.

m_+ and m_-, and γ_+ and γ_-, are the separate cation and anion molalities and activity coefficients. If the molality of A_{v+}, B_{v-} is m, then $m_+ = v_+ m$ and $m_- = v_- m$. A similar definition is used on a concentration scale for the mean ionic concentration $c_\pm$.

(4) The symbol $^\theta$ or $^\circ$ is used to indicate standard. They are equally acceptable.

Name	*Symbol*	*Definition*	*SI unit*	*Notes*
charge number of electrochemical cell reaction	n, ν_e, z		1	(5)
electric potential difference (of a galvanic cell)	$\Delta V, U, E$	$\Delta V = V_R - V_L$	V	(6)
emf, electromotive force	E	$E = \lim_{I \to 0} \Delta V$	V	(7)
standard emf, standard potential of the electrochemical cell reaction	E°	$E = -\Delta_r G^\circ / nF = (RT/nF)\ln K^\circ$	V	(4),(8)
standard electrode potential	E°		V	(4),(9)

(5) n is the number of electrons transferred according to the cell reaction (or half-cell reactions) as written; n is a positive integer.

(6) V_R and V_L are the potentials of the electrodes shown on the right- and left-hand sides, respectively, in the diagram representing the cell. When ΔV is positive, positive charge flows from left to right through the cell, and from right to left in the external circuit, if the cell is short-circuited.

(7) The definition of emf is discussed later in this section. The symbol E_{MF} is no longer recommended for this quantity.

(8) $\Delta_r G^\circ$ and K° apply to the cell reaction in the direction in which reduction occurs at the right-hand electrode and oxidation at the left-hand electrode, in the diagram representing the cell (see later in this section). (Note the mnemonic 'reduction at the right'.)

(9) Standard potential of an electrode reaction, abbreviated as standard electrode potential, is the value of the standard emf of a cell in which molecular hydrogen is oxidized to solvated protons at the left-hand electrode. For example, the standard potential of the $Zn^{2+}|Zn$ electrode, denoted $E^\circ(Zn^{2+}|Zn)$, is the emf of the cell in which the reaction $Zn^{2+}(aq) + H_2 \rightarrow 2H^+(aq) + Zn$ takes place under standard conditions.

Name	*Symbol*	*Definition*	*SI unit*	*Notes*
emf of the cell, potential of the electro-chemical cell reaction	E	$E = E - (RT/nF)\Sigma v_i \ln a_i$	V	(10)
pH	pH	$\mathrm{pH} \approx -\lg\left[\frac{c(\mathrm{H}^+)}{\mathrm{mol\,dm^{-3}}}\right]$	1	(11)
inner electric potential	φ	$\nabla\varphi = -\boldsymbol{E}$	V	(12)
outer electric potential	ψ	$\psi = Q/4\pi\varepsilon_0 r$	V	(13)
surface electric potential	χ	$\chi = \varphi - \psi$	V	
Galvani potential difference	$\Delta\varphi$	$\Delta_\alpha{}^\beta\varphi = \varphi^\beta - \varphi^\alpha$	V	(14)
Volta potential difference	$\Delta\psi$	$\Delta_\alpha{}^\beta\psi = \psi^\beta - \psi^\alpha$	V	(15)

(10) $\Sigma v_i \ln a_i$ refers to the cell reaction, with v_i positive for products and negative for reactants; for the complete cell reaction only mean ionic activities $a_\pm$ are involved.

(11) The precise definition of pH is discussed later is this section. The symbol pH is an exception to the general rules for the symbols of physical quantities in that it is a two-letter symbol and it is always printed in roman (upright) type.

(12) $\boldsymbol{E}$ is the electric field strength within the phase concerned.

(13) The definition is an example specific to a conducting sphere of excess charge Q and radius r.

(14) $\Delta\varphi$ is the electric potential difference between points within the bulk phases α and β; it is measurable only if the phases are of identical composition.

(15) $\Delta\psi$ is the electric potential difference due to the charge on phases α and β. It is measurable or calculable by classical electrostatics from the charge distribution.

Name	*Symbol*	*Definition*	*SI unit*	*Notes*
electrochemical potential	$\tilde{\mu}$	$\tilde{\mu}_B^{\alpha} = (\partial G/\partial n_B^{\alpha})$	J mol^{-1}	(1), (16)
electric current	I	$I = dQ/dt$	A	(17)
(electric) current density	j	$j = I/A$	A m^{-2}	(17)
(surface) charge density	σ	$\sigma = Q/A$	C m^{-2}	
electrode reaction rate constant	k	$k_{ox} = I_a/(nFA\prod_i c_i^{n_i})$	(varies)	(18)
mass transfer coefficient diffusion rate constant	k_d	$k_{d,B} = \lvert \nu_B \rvert I_{l,B}/nFcA$	m s^{-1}	(1)
thickness of diffusion layer	δ	$\delta_B = D/k_{d,B}$	m	(1)
transfer coefficient (electrochemical)	α	$\alpha_c = \frac{-\lvert\nu\rvert RT}{nF}\frac{\partial \ln \lvert I_c\rvert}{\partial E}$	1	(17)
overpotential	η	$\eta = E_I - E_{I=0} - IR_u$	V	
eletrokinetic potential (zeta potential)	ζ		V	
conductivity	κ, (σ)	$\kappa = j/E$	S m^{-1}	(12),(19)
conductivity cell constant	K_{cell}	$K_{cell} = \kappa R$	m^{-1}	

(16) The chemical potential is related to the electrochemical potential by the equation $\mu_B^{\alpha} = \tilde{\mu}_B^{\alpha} - z_B F\varphi^{\alpha}$. For an uncharged species, $z_B = 0$, the electrochemical potential is equal to the chemical potential.

(17) I, j and α may carry one of the subscripts: a for anodic, c for cathodic, e or o for exchange, or l for limiting. I_a and I_c are the anodic and cathodic partial currents. The cathode is the electrode where reduction takes place, and the anode is the electrode where oxidation takes place.

(18) For reduction the rate constant k_{red} can be defined analogously in terms of the cathodic current I_c. For first-order reaction the SI unit is m s^{-1}. n_i is the order of reaction with respect to component i.

(19) Conductivity was formerly called specific conductance.

Name	*Symbol*	*Definition*	*SI unit*	*Notes*
molar conductivity (of an electrolyte)	Λ	$\Lambda_B = \kappa/c_B$	S m^2 mol^{-1}	(1),(20)
electric mobility	u, (μ)	$u_B = v_B/E$	m^2 V^{-1} s^{-1}	(1),(21)
ionic conductivity, molar conductivity of an ion	λ	$\lambda_B = \vert z_B \vert F u_B$	S m^2 mol^{-1}	(1),(22)
transport number	t	$t_B = j_B/\Sigma j_i$	1	(1)
reciprocal radius of ionic atmosphere	κ	$\kappa = (2F^2 I_c/\varepsilon RT)^{1/2}$	m^{-1}	(23)

(20) The unit S cm^2 mol^{-1} is often used for molar conductivity.

(21) v_B is the speed of entities B and E is the electric field strength within the phase concerned.

(22) It is important to specify the entity to which molar conductivity refers; thus for example $\lambda(Mg^{2+}) = 2\lambda(½Mg^{2+})$. It is standard practice to choose the entity to be $1/z_B$ of an ion of charge number z_B, so that for example molar conductivities for potassium, barium and lanthanum ions would be quoted as $\lambda(K^+)$, $\lambda(½Ba^{2+})$, or $\lambda(⅓La^{3+})$.

(23) κ appears in Debye-Hückel theory. The Debye length, $L_D = \kappa^{-1}$, appears in Gouy-Chapman theory, and in the theory of semiconductor space charge. I_c is the ionic strength.

Conventions concerning the signs of electric potential differences, electromotive forces, and electrode potential[24]

(i) The electric potential difference for a galvanic cell

The cell should be represented by a diagram, for example:

$$Zn \,|\, Zn^{2+} \,\vdots\, Cu^{2+} \,|\, Cu$$

A single vertical bar (|) should be used to represent a phase boundary, a dashed vertical bar (¦) to represent a junction between miscible liquids, and double dashed vertical bars (¦¦) to represent a liquid junction in which the liquid junction potential is assumed to be eliminated. The electric potential difference, denoted ΔV or E, is equal in sign and magnitude to the electric potential of a metallic conducting lead on the right minus that of a similar lead on the left. The emf (electromotive force), also usually denoted E, is the limiting value of the electric potential difference for zero current through the cell, all local charage transfer equilibria and chemical equilibria being established. Note that the symbol E is often used for both the potential difference and the emf, and this can sometimes lead to confusion.

When the reaction of the cell is written as

$$\tfrac{1}{2}Zn + \tfrac{1}{2}Cu^{2+} = \tfrac{1}{2}Zn^{2+} + \tfrac{1}{2}Cu, \qquad n = 1$$

or

$$Zn + Cu^{2+} = Zn^{2+} + Cu, \qquad n = 2,$$

this implies a cell diagram drawn, as above, so that this reaction takes place when positive electricitiy flows through the cell from left to right (and therefore through the outer part of the circuit form right to left). In the above example the right-hand electrode is positive (unless the ration $[Cu^{2+}]/[Zn^{2+}]$ is extremly small), so that this is the direction of spontaneous flow if a wire is connected across the two electrodes. If, however, the reaction is written as

$$\tfrac{1}{2}Cu + \tfrac{1}{2}Zn^{2+} = \tfrac{1}{2}Cu^{2+} + \tfrac{1}{2}Zn, \qquad n = 1$$

or

$$Cu + Zn^{2+} = Cu^{2+} + Zn, \qquad n = 2,$$

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(24) These are in accordance with the 'Stockholm Convention' of 1953

this implies the cell diagram

$$Cu \,|\, Cu^{2+} \,\vdots\, Zn^{2+} \,|\, Zn$$

and the electric potential difference of the cell so specified will be negative. Thus a cell diagram may be drawn either way round, and correspondingly the electric potential difference appropriate to the diagram may be either positive or negative.

(ii) Electrode potential (potential of an electrode reaction)

The so-called electrode potential of an electrode is defined as the emf of a cell in which the electrode on the left is a standard hydrogen electrode and the electrode on the right is the electrode in question. For example, for the silver/silver chloride electrode (written $Cl^-(aq) \,|\, AgCl \,|\, Ag$) the cell in question is

$$Pt \,|\, H_2(g, p = p°) \,|\, HCl(aq, a_\pm = 1) \,\vdots\, HCl(aq, a_\pm') \,|\, AgCl \,|\, Ag$$

A liquid junction will be necessary in this cell whenever $a_\pm'$(HCl) on the right differs from $a_\pm$(HCl) on the left. The reaction taking place at the silver/silver chloride electrode is

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$$

The complete cell reaction is

$$AgCl(s) + \tfrac{1}{2}H_2(g) \rightarrow H^+(aq) + Cl^-(aq) + Ag(s)$$

In the standard state of the hydrogen electrode, $p(H_2) = p° = 10^5$ Pa and $a_\pm$(HCl) = 1, the emf of this cell is the electrode potential of the silver/silver chloride electrode. If, in addition, the mean activity of the HCl in the silver/silver chloride electrode $a_\pm$(HCl) = 1, then the emf is equal to E for this electrode. The standard electrode potential for $HCl(aq) \,|\, AgCl \,|\, Ag$ has the value E = +0.222 17 V at 298.15 K. For p = 101 325 Pa the standard potential of this electrode (and of any electrode involving only condensed phases) is higher by 0.17 mV; i.e.

$$E°(101\,325 \text{ Pa}) = E°(10^5 \text{ Pa}) + 0.17 \text{ mV}$$

A compilation of standard electrode potentials, and their conversion between different standard pressures, can be found in PAC 63 (1991) 569-596. Notice that in writing the cell whose emf represents an electrode potential, it is important that the hydrogen electrode should always be on the left.

(iii) Operational definition of pH

The notional definition of pH given in the table above is in practice replaced by the following operational definition. For solution X the emf E(X) of the galvanic cell

reference	KCl(aq,	‖	solution X	H_2(g)	Pt
electrode	$m > 3.5$ mol kg^{-1})	‖			

is measured, and likewise the emf E(S) of the cell that differs only by the replacement of the solution X of unknown pH(X) by the solution S of standard pH(S). The unknown pH is then given by

$$pH(X) = pH(S) + (E_S - E_X)F/(RT\ln 10)$$

Thus defined, pH is dimensionless. Values of pH(S) for several standard solutions and temperatures are listed in PAC 37 (1985) 531-542. The reference value pH standard is an aqueous solution of potassium hydrogen phthalate at a molality of exactly 0.05 mol kg^{-1}: at 25°C (298.15K) this has a pH of 4.005.

In practice a glass electrode is almost always used in place of the Pt|H_2 electrode. The cell might then take the form

reference	KCl(aq,	‖	solution X	glass	H^+,Cl^-	AgCl	Ag
electrode	m>3.5 mol kg^{-1}	‖					

The solution to the right of the glass electrode is ususally a buffer solution of KH_2PO_4 and Na_2HPO_4, with 0.1 mol dm^{-3} of NaCl. The reference electode is usually a calomel electode, silver/silver chloride electrode, or a thallium amalgam/thallous chloride electrode. The emf of this cell depends on $a(H^+)$ in the solution X in the same way as that of the cell with the Pt|H_2 electrode, and thus the same procedure is followed.

In the restricted range of dilute aqueous solutions having amount concentrations less than 0.1 mol dm^{-3} and being neither strongly acidic nor strongly alkaline ($2 < pH < 12$) the above definition is such that

$$pH = -\lg[\gamma_{\pm} c(H^+)/\text{mol dm}^{-3})]\pm 0.02,$$

$$= -\lg[\gamma_{\pm} m(H^+)/\text{mol dm}^{-3})]\pm 0.02,$$

where $c(H^+)$ denotes the amount concentration of hydrogen ion H^+ and $m(H^+)$ the corresponding molality, and $\gamma_{\pm}$ denotes the mean ionic activity coefficient of a typical uni-univalent electolyte in the solution on a concentration basis or a molality basis as appropriate.

For further information on the definition of pH see PAC 37 (1985) 531-542.