

1.0 Fundamentals

This chapter introduces the electrochemical cell, its components, basic definitions, and the processes that take place during electrolysis. The difference between thermodynamics and kinetics is explained through the concepts of reduction potential and overpotentials.

1.1 The electrochemical cell

Consider the electrochemical cell shown below where the electrolyte is stagnant. It consists of zinc and copper electrodes immersed in solutions of ZnSO_4 and CuSO_4 respectively. The two electrodes are connected through a metal wire (see Fig. 1.1).

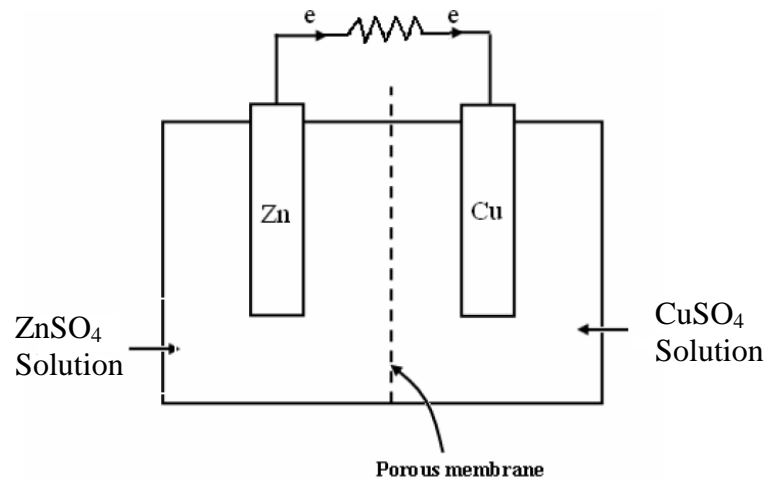


Fig. 1.1. Schematic diagram of an electrochemical cell.

A porous membrane is used to prevent mixing of the electrolyte. Electrons are produced in one electrode, which corresponds to the dissolution of Zn:



These electrons are transferred to the other electrode through an electrical conductor and are consumed by the reaction, which corresponds to the deposition of Cu:



The electrode where dissolution (or oxidation because of increase in the oxidation number) of Zn takes place is called the anode, while the electrode where deposition (or reduction because of decrease in the oxidation number) of Cu takes place is called the cathode. Reactions 1 and 2 individually are called half-cell reactions; together they are also called, for obvious reasons, redox reactions. In an electrochemical cell, a minimum of two half cell reactions must occur, one at the cathode and one at the anode. Electrolyte in anode and cathode chamber in cells with diaphragms/separators is called anolyte and catholyte respectively.

For electrochemical reactions to occur, reactants must exist in a charged or ionized state. Ionization can be achieved by either dissolving metal compounds in solvents such as water and molten salts. For example, (i) Cu and Zn are electrodeposited from aqueous solutions of CuSO_4 and ZnSO_4 respectively and (ii) aluminium is electrodeposited from Al_2O_3 dissolved in a molten salt, cryolite (Na_3AlF_6).

1.1.1 Mass transfer of ions

Let us now look closely at the ionic activity at the anode-electrolyte interface (AEI) and the cathode/electrolyte interface (CEI) in Fig. 1.1. Accumulation of Zn^{2+} takes place at the AEI because of the dissolution of Zn. Very soon the anode will be completely surrounded by Zn^{2+} . Similarly, the copper deposition reaction will gradually deplete Cu^{2+} at the CEI, ultimately resulting in a situation where there is no Cu^{2+} at the CEI. Consequently, the Zn dissolution reaction would stop at the anode since the newly-formed Zn^{2+} would be repelled by the Zn^{2+} surrounding the anode. The absence of Cu^{2+} at the CEI means the copper deposition reaction will stop. That is, after a “short” while, the half-cell reactions should come to a grinding halt. However, it has been observed that the redox reactions continue in the galvanic cell till the complete dissolution of the Zn anode. How do we explain this paradox? Clearly forces must be acting in the electrolyte to ensure that Zn^{2+} is continuously transported from the AEI to the bulk electrolyte. Similarly, Cu^{2+} must be transported from the bulk electrolyte to the CEI for the cathodic half cell reaction to continue. A follow-up question therefore arises: What are the mechanisms for the transport of Zn^{2+} and Cu^{2+} ? There are three, namely, electromigration, diffusion and natural convection. In electromigration, the cations and anions move parallel and anti-parallel to the direction of the electric field, as shown in Fig. 1.2a. Diffusion causes movement of ions from regions of higher to lower concentrations (see Fig. 1.2b). Natural convection occurs because of density difference between the electrolyte at the AEI (or CEI) and bulk electrolyte. Because of the higher Zn^{2+} concentration at the AEI, the density of electrolyte at the AEI is greater than the bulk anolyte density. This causes the electrolyte near the AEI to “sink;” liquid rushes from the bulk to fill the “void” resulting in a counter-clockwise circulation of anolyte, as shown in Fig. 1.3. The topic on mass transfer will explain the different mechanisms of mass transfer and how they affect electrolysis.

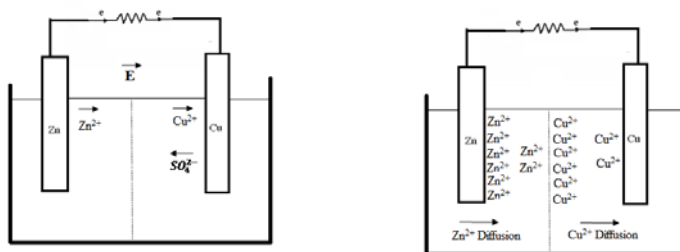


Fig. 1.2. Electrochemical cell depicting transport of ions by (a) electromigration and (b) diffusion. The arrows show the direction of electric field and motion of ions.

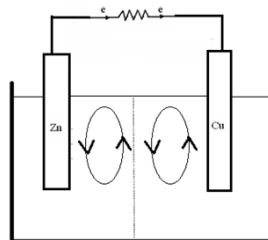


Fig. 1.3. Natural convection in an electrochemical cell.

In many cases, as will be shown later, mass transport of ions is the rate controlling step in commercial redox reactions, be it in electrowinning of metals or in galvanic cells. This results in the concept of the limiting current density, which is the maximum current that can flow through a cell. To further speed up the transport of ions, forced convection is also used, for example by sparging the electrolyte with air bubbles.

Another phenomenon occurs as the redox reactions continue. Positive charge builds up in the anolyte due to the generation of Zn^{2+} by the anodic reaction. Similarly, the catholyte becomes progressively negative as Cu^{2+} is consumed by the cathodic reaction. However, even though ions exist in bulk solution, the solution itself is always electroneutral. Consequently, two events occur simultaneously to neutralize the charged electrolyte: (i) Zn^{2+} will be transported towards the catholyte and (ii) SO_4^{2-} will move towards the anolyte. The electroneutrality equation is:

$$\sum z_i C_i = 0 \quad (1.3)$$

Here z_i and C_i are charge and concentration of ion “ i ” respectively. z_i is negative for anions and positive for cations. In reality, the electrolyte is not “truly” neutral. There is an electric double layer as both the AEI and the CEI are charged, but it is usually ignored since its dimension (of the order of nm) is much smaller than the extent of the bulk electrolyte. The charged electrode/electrolyte interface, however, has a significant effect on the kinetics and occurrence of half-cell reactions and will be discussed separately in a following chapter.

As a consequence of ion transport due to electroneutrality considerations, an interesting question arises because of the presence of Zn^{2+} in the anolyte: Will Zn co-deposit with Cu at the cathode? Again, this important question will be discussed in later chapters.

The transport of ions in the electrolyte raises another fascinating point. Is there a correlation between the rates of electron flow between the metallic wire joining the electrode and the rate of transport of ions? A charge balance in the copper deposition reaction suggests that the rate of flow of electrons in the circuit has to be equal to the rate of flow of ionic charge through Cu^{2+} . Here two electrons/time flowing to the cathode requires the consumption and hence transport of 1 Cu^{2+} /time. Since the electrons for the deposition of copper comes from the anode, the implicit consequence is that the rate of the anodic and cathodic reactions must be equal. To understand this phenomenon, let us assume that the rate of the anodic reaction is faster than the rate of the cathodic reaction. Accordingly, electrons are being pumped to the cathode at a higher rate than it can be consumed at the cathode, resulting in increasing accumulation of electrons in the cathode. This will result in the cathode becoming progressively more negative, which, in turn, will oppose further transport of electrons from the anode to the cathode. Consequently, the rate of the anodic reaction will gradually slow down until its rate becomes equal to the cathodic reaction, after which the anodic and cathodic reactions will proceed at the same slower rate.

1.1.2 Faraday’s law

The rate of half cell reactions is given by Faraday’s law, which states that a charge corresponding to one Faraday (96500 C) results in the electrolytic production (or consumption) of one gram equivalent of species in a half cell reaction. This law is easy to implement in the case of a half cell reaction such as $\text{Cu}^{2+} + 2e = \text{Cu}$. Here, 96500 C produces 1 gram equivalent of Cu (atomic weight of Cu/valency), that is, 65/2 g of Cu. However, as a rule it is much easier to see Faraday’s law in terms of reaction stoichiometry since the concept of gram equivalent can be confusing to “non-chemists.” For example, how do we determine the molar rate of (i) oxygen or H^+ produced or (ii) H_2O consumed by the half cell reaction: $2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4e$. By following reaction stoichiometry, we can simply say:

- Charge corresponding to 4 moles of electrons ($4F = 4 \times 96500 = 3.86 \times 10^5$ C) produces one mole of oxygen.
- 3.86×10^5 C produces 1 mole of O_2 .
- 3.86×10^5 C produces 4 moles of H^+ .
- 3.86×10^5 C consumes 2 moles of H_2O .

1.1.3 Classification of electrolysis cells

There are two types of electrolysis cells. In the first type, current spontaneously flows between the electrodes once they are joined by a metal wire. That is, once the electrodes are electronically connected, the redox reactions occur spontaneously. In essence, these cells produce electrical energy and are known as galvanic cells, a prominent example of which is batteries. The phenomenon of corrosion also occurs by the formation of a galvanic cell between the corroding metal and its moist environment.

The second type of cells requires the application of a voltage for the redox reactions to occur. These cells are used for the deposition of metals, production of gases such as chlorine, hydrogen etc. For metal deposition reactions at the cathode, these cells are further classified as electrowinning and electrodeposition cells. Electrowinning is used for the bulk production of metals from leach liquor obtained from the hydrometallurgical processing of metallic ores. Electrowinning cells are used for the production of a number of primary metals such as Cu, Zn, Ni, and Al. Electrodeposition cells are used for depositing small quantities of metals on to a substrate for altering their surface properties such as increasing corrosion and abrasion resistance, or simply for aesthetics, as in the gold plating of silver jewellery. Hereafter, for fundamental considerations, unless specifically stated, electrodeposition cells and electrowinning cells will be used interchangeably.

1.1.4 Cell voltage

For current to flow in the circuit, a potential (voltage) difference must exist between the two electrodes. In galvanic cells, the half cell reactions occur spontaneously and a potential difference is automatically set-up once the electrodes are connected. In electrowinning cells an external potential difference must be applied for the half cell reactions to occur. Two questions therefore arise:

- What is the voltage that we can obtain from a galvanic cell given specific anode and cathode materials?
- What is the voltage that needs to be applied in an electrowinning cell?

There are two approaches for determining the cell voltage. One can take all possible combinations of electrodes, make the cells and then measure the voltage between the electrodes, an unenviably tedious job. Alternately, one can measure the potential of a half-cell reaction, known as the half cell potential, such as those given by equations 1.1 and 1.2. By half cell potential of equation 1, we mean the potential difference that occurs between a Zn electrode and the solution containing Zn^{2+} . Or, the potential difference between the Cu electrode and the solution containing Cu^{2+} . Cell voltage can then be determined by adding the half cell potentials of the appropriate anodic and cathodic half-cell reactions. However, before we proceed with this approach, there is a need to first understand the origin of half cell potential, its definition, and the manner in which it is measured.

1.2 Thermodynamics

This section discusses the origin of the half cell potential and introduces the notion and methodology for determining standard and non-standard reduction potentials.

1.2.1 Origin of half cell potential

To understand the origin of half cell potential, consider a Cu electrode which is immersed in a solution of CuSO_4 . You can check that the electrode weight remains unchanged with time. This suggests that the two possible reactions: (i) $\text{Cu}^{2+} + 2\text{e} \rightarrow \text{Cu}$ (deposition), and (ii) $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}$ (dissolution) occur at the same rate. However this equilibrium state is not achieved instantaneously. When the Cu electrode is immersed, both the dissolution and deposition reactions can occur. Now assume that the

dissolution reaction is faster than the deposition reaction. For example, 6 Cu^{2+}/s are depositing as Cu and 8 Cu atom/s are dissolving as Cu^{2+} . The net effect is that 2 moles/s of Cu from the electrode dissolves in the electrolyte as Cu^{2+} . Consequently, at the end of the 1st second, there are 4 excess electrons in the metal side of the metal/electrolyte interface (MEI) and 4 excess positive charges – due to 2 excess Cu^{2+} -- on the solution side of the MEI. These excess charges line up in parallel, shown in Fig. 1.4 below, resulting in the formation of an electric double layer (EDL) at the MEI.

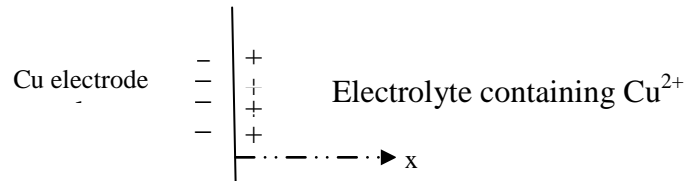


Fig. 1.4. Electric double layer at a metal-electrolyte interface.

The double layer electric field will retard the motion of Cu^{2+} in +x direction and speed up Cu^{2+} in the – x direction. In the 2nd second, therefore, the rate of dissolution Cu atoms will decrease to, say 7 Cu^{2+}/s . Simultaneously, the electric field will hasten the transport of Cu^{2+} from the bulk to the interface and hence increase the rate of the deposition reaction. Since the charge on the solution side of the double layer will now become less positive, thereby reducing the double layer charge, which, in turn, will again speed up the dissolution reaction and slow down the deposition reaction. Competition between the dissolution and deposition reactions will continue until equilibrium is established, leading to the formation of a stable double layer of charge. This equilibrium double layer, which acts like a capacitor, gives rise to the half cell potential, which is also referred to as electrode-solution potential. In general, some metals have a greater inclination to stay in solution as ions, that is, in their oxidized state. Other metals may prefer to stay as the metal phase, that is, in their reduced state. The sign of the electric field in the double layer depends on the natural tendency of metal to be in its ionic or metallic state. For reaction 1, since Zn has a tendency to dissolve, the EDL will have positive charge in the electrode and negative charge in the electrolyte.

Electric double layer is a feature of all fluid-solid interfaces, irrespective of whether the solid is a conductor, semi-conductor, or insulator. For the same fluid, say water, the magnitude of the potential drop across the EDL will be highest for a good conductor such as a metal. Bockris et al. provide a deep and insightful discussion on EDLs.

1.2.2 Measurement of Half-Cell Potential

We know from electrical engineering that potential is always measured relative to the “earth,” which is for convenience, assigned zero potential. The electrochemical analog of “earth” is the hydrogen evolution reaction: $\text{H}^+ + \text{e} = 0.5 \text{H}_2$, which has been assigned a standard half cell potential of zero. The half cell potential of all other reactions is measured with respect to the H_2 evolution reaction; such a cell is shown below, in Fig. 1.5. The cell consists of the metal whose standard half cell potential (for the reaction $\text{M}^{n+} + \text{ne} = \text{M}$) is to be determined. The hydrogen evolution reaction occurs at the platinum electrode.

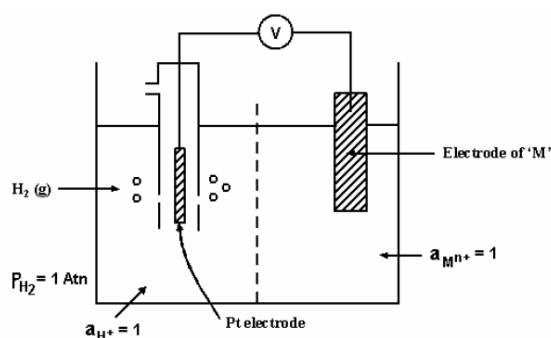


Fig. 1.5. Configuration of an electrochemical cell for measuring the standard half cell potential for the reaction $M^{n+} + ne = M$.

The standard half-cell reduction potential (E°) is defined when (i) activity of H^+ and $M^{n+} = 1$, (ii) $p_{H_2} = 1$ atm, and (iii) temperature = $25^{\circ}C$.

Please remember that the half cell reduction potential is an equilibrium quantity when the metal is in equilibrium with its ion in solution. A snapshot of the electrochemical series, which lists the reduction potential of different half-cell reactions, is given in Table 1.1.

Table 1.1. A snapshot of the electrochemical series showing the standard reduction potentials

| Electrode reaction (M^{n+}/M) | E° (V) |
|-----------------------------------|-----------------|
| $Li^+ + e = Li$ | -3.01 |
| $Ba^{2+} + 2e = Ba$ | -2.92 |
| $Mg^{2+} + 2e = Mg$ | -2.38 |
| $Zn^{2+} + 2e = Zn$ | -0.76 |
| $H^+ + e = 0.5 H_2$ | 0.0 |
| $Cu^{2+} + 2e = Cu$ | 0.34 |
| $Fe^{3+} + e = Fe^{2+}$ | 0.77 |
| $Ag^+ + e = Ag$ | 0.81 |
| $O_2 + 4H^+ + 4e = 2H_2O$ | 1.34 |

The meaning of the sign of E° can be obtained from the relationship: $\Delta G^{\circ} = -nFE^{\circ}$. Clearly M^{n+}/M reactions that have a negative E° will tend to have the metal, M in its ionic (dissolved) state. Similarly M^{n+}/M reactions that have a positive E° will tend to deposit M from a solution containing M^{n+} . Unless otherwise stated the symbol E° will represent reduction potential. Reduction potential may also, at places, be explicitly stated as $E^{\circ}(M^{n+}/M)$. During the measurement of reduction potentials, there is no current flowing through the cell since the voltmeter has a very high resistance. That is, no net half cell reaction is taking place at the electrodes. Reduction potentials, standard or non-standard, therefore represent a state of equilibrium and hence are thermodynamic quantities.

It should also be noted that it is not necessary that M^{n+}/M reactions with negative (positive) reduction potential will always have the metal in its ionic state. For example, if we set up a galvanic cell consisting of Ba and Zn electrodes immersed in $BaSO_4$ and $ZnSO_4$ respectively, then Ba will be the anode and Zn will be the cathode; the anodic and cathodic reactions being $Ba = Ba^{2+} + 2e$ and $Zn^{2+} + 2e = Zn$ respectively. Hence the reduction potential is a reflection of the relative tendency of a metal M_1 to stay in a metallic or ionic state with respect to another metal M_2 .

Another important point is that a metal M can exist as different ions in solutions of different pH and each metal-metal ion pair will have a different reduction potential. For example, in acidic solutions, Zn^{2+} is present, while ZnO_2^{2-} exists in strongly basic solution. The standard reduction potential of the

half cell reaction $\text{ZnO}_2^{2-} + 2\text{H}_2\text{O} + 2\text{e} = \text{Zn} + 4\text{OH}^-$ is -1.215 V compared to -0.76 volts for the $\text{Zn}^{2+} + 2\text{e} = \text{Zn}$ reaction.

1.2.3 Reference electrodes (RE)

It is not convenient to use a standard hydrogen electrode (SHE) for experiments. We need compact and portable reference electrodes, examples of which are the standard calomel electrode (SCE) and Ag/AgCl electrode. The half cell potential of each of these REs is defined with respect to SHE. For example,

$$E^\circ(\text{SCE}) = +0.242 \text{ V with respect to SHE}$$

The USP of reference electrodes is that their potential does not change with current, an important characteristic that will be clear in the chapter on electrochemical experiments.

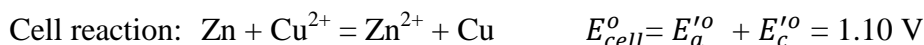
1.2.4 Calculation of E_{cell}°

Now that we know the half cell reduction potentials, how do we calculate the potential of an electrochemical cell (or, the redox potential), E_{cell}° . There is more than one way of calculating E_{cell}° . We will follow the simpler method, which does not require memorizing the formula for E_{cell}° . The following steps should be followed:

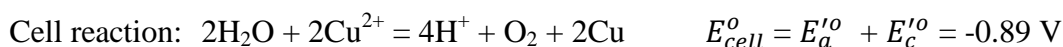
- Write the anodic and cathodic reactions as they occur, that is, oxidation reaction at the anode and reduction reaction at the cathode.
- Write down the "actual" standard half cell potentials of the anodic and cathodic reaction, defined as $E_a^{\prime\circ}$ and $E_c^{\prime\circ}$ respectively. Let us assume metal M_1 is oxidized at the anode and metal M_2 is reduced at the cathode. Then $E_a^{\prime\circ} = -E^\circ(\text{M}_1^{\text{n}+}/\text{M}_1)$ and $E_c^{\prime\circ} = E^\circ(\text{M}_2^{\text{n}+}/\text{M}_2)$.
- $E_{\text{cell}}^\circ = E_a^{\prime\circ} + E_c^{\prime\circ}$

To illustrate the method for calculating E_{cell}° , consider the following examples of a Cu/Zn galvanic cell and electrowinning of copper

Cu/Zn galvanic cell



Electrowinning of Cu



One can also represent E_{cell}° purely in terms of reduction potential. For the overall reaction $\text{Zn} + \text{Cu}^{2+} = \text{Zn}^{2+} + \text{Cu}$, $E_{\text{cell}}^\circ = E^\circ(\text{Cu}^{2+}/\text{Cu}) - E^\circ(\text{Zn}^{2+}/\text{Zn})$. That is, $E_{\text{cell}}^\circ = \text{reduction potential of cathodic reaction} - \text{reduction potential of anodic reaction}$.

It is not important which convention you choose, but you must be consistent. One major problem for students in electrochemistry is messing up the sign (- or +) of potentials, as will be evident later. It is recommended that the method suggested in the beginning of this section may be followed.

Please note that E_{cell}° is not a reduction or oxidation potential. It represents the potential for the overall reaction the way it is written. For example,

➤ $E_{cell}^{\circ} = -0.89$ V represents the overall reaction $2\text{H}_2\text{O} + 2\text{Cu}^{2+} = 4\text{H}^+ + \text{O}_2 + 2\text{Cu}$. For the reaction, $4\text{H}^+ + \text{O}_2 + 2\text{Cu} = 2\text{H}_2\text{O} + 2\text{Cu}^{2+}$, $E_{cell}^{\circ} = +0.89$ V.

1.2.5 Reaction multiplication and E°

To get the cell reaction, we have to equate the number of electrons involved in both the anodic and cathodic reactions, which, in turn, requires multiplying either one or both half cell reactions with different integers. For example, in the electrowinning of copper, the cathodic reaction has to be multiplied by 2. This raises the question: Do the following reactions have the same E° ?

1. $\text{Cu}^{2+} + 2\text{e} = \text{Cu}$
2. $2\text{Cu}^{2+} + 4\text{e} = 2\text{Cu}$

Using the relationship, $\Delta G^{\circ} = -nFE^{\circ}$, you can show that E° for reactions 1 and 2 are same. In reactions 1 and 2 “n” is 2 and 4 respectively. In essence, multiplying a half cell reaction, say, by 2, doubles the value of ΔG° , but leaves E° unchanged.

1.2.6 Significance of sign of E_{cell}°

What is the significance of the sign of E_{cell}° ? Again from the relationship, $\Delta G_{cell}^{\circ} = -nFE_{cell}^{\circ}$, a positive E_{cell}° implies that the half-cell reactions will occur spontaneously if the electrodes are connected with a metallic wire, much like a battery. That is, the cell acts as a source of electrical energy. Similarly, a negative E_{cell}° implies that energy has to be applied for the half-cell reactions to occur, as in electrowinning or electrodeposition cells.

Another point of confusion is “n,” the number of electrons in a cell reaction. It is easy to define “n” for a half cell reaction, but slightly confusing for the overall (cell) reaction because the electrons are absent in the latter. For a cell reaction, n refers to the number of electrons one gets after multiplying the half cell reactions with integers to ensure that the number of electrons are same in both the anodic and cathodic reaction. For example, in the copper electrowinning reaction, $n = 2$ for the cathodic reaction, but $n = 4$ for the cell reaction.

1.2.7 Half-cell/cell potential under non-standard conditions

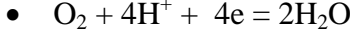
E° for a half cell reaction corresponds to standard conditions, that is (i) $a_{M^{n+}} = 1$, (ii) $T = 298$ K, and (iii) for reactions involving gases, the partial pressure of the gas should be 1 atm. How do we determine the reduction potential, E , under non-standard conditions, that is when ionic activities or temperature or gas partial pressures are different from those under standard conditions? Here we use the Nernst equation.

- The Nernst equation can be written either for calculating non-standard (i) half-cell reduction potentials or (ii) cell reduction potentials, E_{cell}^1 . The Nernst equation for the $\text{Cu}^{2+} + 2\text{e} = \text{Cu}$ reaction is given in equation 1.4.

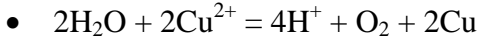
¹ Another frequently used term is Decomposition Potential, the potential above which the current rises appreciably. The magnitude of decomposition potential is greater than E_{cell} for electrowinning cells.

$$E \left(\text{Cu}^{2+} / \text{Cu} \right) = E^o \left(\text{Cu}^{2+} / \text{Cu} \right) - \frac{RT}{2F} \left[\ln \frac{a_{\text{Cu}}}{a_{\text{Cu}^{2+}}} \right] = 0.34 - \frac{RT}{2F} \left[\ln \frac{a_{\text{Cu}}}{a_{\text{Cu}^{2+}}} \right] \quad (1.4)$$

where, $a_{\text{Cu}^{2+}}$ is the activity of Cu^{2+} in the electrolyte., T is the temperature (in K) and F = 96500 C.
 $a_{\text{Cu}} = 1$ for pure copper.



$$E \left(\text{O}_2 / \text{H}_2\text{O} \right) = E^o \left(\text{O}_2 / \text{H}_2\text{O} \right) - \frac{RT}{2F} \left[\ln \frac{1}{P_{\text{O}_2} a_{\text{H}^+}^4} \right] = 1.23 - \frac{RT}{2F} \left[\ln \frac{1}{P_{\text{O}_2} a_{\text{H}^+}^4} \right] \quad (1.5)$$



$$E_{\text{cell}} = E_{\text{cell}}^o - \frac{RT}{4F} \left[\ln \frac{P_{\text{O}_2} a_{\text{H}^+}^4}{a_{\text{Cu}^{2+}}^2} \right] \quad (1.6)$$

Please note that activity and concentration are also represented by curly and square brackets respectively. For example,

$$a_{\text{Cu}^{2+}} = \{ \text{Cu}^{2+} \} = \gamma_{\pm} [\text{Cu}^{2+}]$$

$\{ \text{Cu}^{2+} \}$ = activity of Cu^{2+}
 $[\text{Cu}^{2+}]$ = concentration of Cu^{2+}

Since activity of an ion cannot be measured, define γ_{\pm} , the mean ionic activity of the salt, in this case CuSO_4 , in the electrolyte.

Unit of concentration is molality (moles/kg solvent), but usually, with little error, **molarity** (moles/litre) can be used as a unit of concentration.

1.2.8 Determination of γ_{\pm}

γ_{\pm} be determined by using the Debye-Huckel equation:

$$\log \gamma_{\pm} = -A |z_+ z_-| I^{0.5} \quad (1.7)$$

A = 0.509 for H_2O at 25 C, z_+ and z_- are the valence of the cation and anion respectively that constitute the salt.

$$I = \text{Ionic strength} = 0.5 \sum C_i z_i^2 \quad (1.8)$$

Equation 1.8 holds good for $I \leq 10^{-3}$ M

At higher concentrations use the “extended” Debye Huckel Law

$$\log \gamma_{\pm} = \frac{-A |z_+ z_-| I^{0.5}}{1 + I^{0.5}} \quad (1.9)$$

1.2.9 Limitations of E/E^o

E/E^o has been measured under equilibrium conditions, i.e., when there is no net current flowing through the cell. This implies, for example, that there is no net metal dissolution taking place at the

anode or metal deposition taking place at the cathode. In real-life situations, we would like to operate electrolytic cells at finite currents because productivity is proportional to the current flowing through the cell.

In general, the applied voltage $V_{cell} \neq E_{cell}$

Electrowinning cells: $V_{cell} > E_{cell}$

$$\text{Cu: } |E_{cell}| = 0.89\text{V} ; V_{cell} \approx 2\text{V}$$

$$\text{Al: } |E_{cell}| = 1.2\text{V}; V_{cell} = 4.5 \text{ V}$$

Galvanic cells: $V_{cell} < E_{cell}$

$$V_{cell} (\text{Zn-C battery}) < 1.5 \text{ V}$$

In electrowinning cells, a voltage higher than E_{cell} has to be applied, that is more energy than what is dictated by thermodynamics has to be supplied, for example in depositing copper. Similarly, we will be drawing lower voltages than E_{cell} in a battery. Hence it appears that E_{cell} is not relevant in real-life applications. This is not true because E_{cell} acts as a **benchmark**, that is, it can be taken as a measure of the extent of "non-ideal" performance, or voltage efficiency, of an electrolytic cell. Voltage efficiency is related to the energy efficiency of a cell and will be discussed in a later chapter. Voltage efficiency is defined as:

- Electrowinning cell: Voltage efficiency = $\frac{E_{cell}}{V_{cell}} \times 100$
- Galvanic cell: Voltage efficiency = $\frac{V_{cell}}{E_{cell}} \times 100$

1.3 Why is V_{cell} different from E_{cell} ?

V_{cell} is different from E_{cell} because the flow of current leads to the phenomenon of "polarization" for each half-cell reaction. Polarization manifests itself as an "overpotential," that is, an additional potential drop over and above the half-cell reduction potential. There are three types of polarization:

- Activation polarization** represents the resistance to half-cell reaction occurring at an electrode and is akin to the concept of activation energy in the case of pure chemical reactions. That is, there is an activation energy associated with half cell reactions at both the anode and the cathode. However, the presence of an electric double layer adjacent to an electrode makes an electrochemical reaction different from a chemical reaction. This electric field can either oppose or aid the motion of the ion towards or away from the electrode depending on whether the ion is an anion or a cation. For example, consider the half-cell reaction $\text{Cu}^{2+} + 2e = \text{Cu}$ at the cathode. Activation polarization has two components here, namely, (i) the energy involved in transporting Cu^{2+} across the EDL and (ii) activation energy for the copper reduction reaction to occur. In this case, the electric field in the EDL points towards the cathode and hence it aids the transport of Cu^{2+} towards the cathode. To visualize the effect of EDL assume that the Cu electrode in Fig. 1.4 is the cathode. Thus activation overpotential at the cathode (η_a^c) represents the extra energy required for the half-cell reaction to occur at the cathode. Similarly, one can define the activation overpotential at the anode, η_a^a .

One can clearly see the adverse impact of activation polarization; it increases the voltage or, in other words, energy consumption for a given value of current. Fortunately, as will be shown later, this concept can also be used to eliminate unwanted reactions, for example the evolution of H_2 during the electrowinning of Zn.

- b) **Concentration polarization** occurs when mass transfer of reacting/product ions cannot keep pace with rate of electron transfer, that is, current. For example, consider the cathode during the electrowinning of copper. Let us say current is flowing at a constant rate of $10 \text{ e}^-/\text{s}$. Since electrons cannot accumulate at the cathode, $5 \text{ Cu}^{2+}/\text{s}$ are being continuously supplied from the bulk electrolyte to the cathode. The transport of Cu^{2+} depends on the mass transport mechanism, namely, diffusion, convection, and migration. Now let us say, we increase the current to $12 \text{ e}^-/\text{s}$. However, since flow conditions in the electrolyte are unchanged, $5 \text{ Cu}^{2+}/\text{s}$ are still coming to the cathode. Since we are operating under constant current conditions, and there can be no accumulation of electrons, the potential goes up at the cathode, which, in turn, increases the transport of Cu^{2+} to $6/\text{s}$ by enhancing the effect of migration and diffusion². Concentration overpotential is associated, like activation overpotential, with both the anodic (η_a^a) and cathodic (η_c^c) reactions.

Concentration polarization has adverse and beneficial effects, much like activation overpotential. In addition, as will be shown later, it affects the quality of the deposit. Moreover, the concept of concentration overpotential is also used to define the maximum permissible current flow in an electrolytic cell.

- c) **Resistance polarization** is due the passage of current through all the resistive components of the cell, namely the electrode, connecting wire, and the electrolyte. It manifests as the **IR drop** in the cell, the predominant component of which is due to the electrolyte resistance, R_e .

1.4 Voltage balance

1.4.1 Electrowinning cell

The sign of the activation and concentration overpotentials at the electrodes are given below:

- $\eta_a^a, \eta_c^a \rightarrow$ positive
- $\eta_a^c, \eta_c^c \rightarrow$ negative

However, since all overpotentials have the effect of increasing the applied potential, we take the absolute values of activation and concentration overpotentials at the anode. Both η_a & η_c depend on current density, $i = I/A$ (A/m^2), where I is the cell current and A is the submerged electrode area. For η_a^a, η_c^a , A refers to the anode area. Similarly, for η_a^c, η_c^c , A refers to the cathode area.

$$V_{cell} = |E_{cell}| + \eta_a^a + |\eta_a^c| + \eta_c^a + |\eta_c^c| + IR_e \quad (1.10)$$

Equation 1.10 simply states that for electrowinning cells, the applied voltage increases with current. Thus overpotentials can also be viewed as a source of voltage drop, much like electrolyte resistance. In a sense, one can visualize electrochemical cells as an electrical circuit with several resistances in series; they do not matter as long as there is no current flow through the cell. However, during electrolysis, these resistances result in additional voltage drops.

Industrial electrochemical cells can be operated under two modes: (i) constant current or galvanostatic and (ii) constant voltage or potentiostatic. Overpotentials would result in higher V_{cell} in the

² The increase in electric field with cell voltage is obvious as the magnitude of the electric field is proportional to potential gradient, which increases with increasing V_{cell} . However, the effect of increasing cell voltage on diffusion is not obvious and will be discussed in the chapter on concentration overpotential.

galvanostatic mode and lower cell current in the potentiostatic mode, conclusions that be verified from the voltage balance equation stated above.

1.4.2 Galvanic Cell

Equation 1.11 shows the voltage balance in a galvanic cell, for example a battery used in torch or a cell phone.

$$V_{cell} = |E_{cell}| - \eta_a^a - |\eta_a^c| - \eta_c^a - |\eta_c^c| - IR_e \quad (1.11)$$

Here the voltage written on the battery is E_{Cell} . When current is drawn from the battery to light a torch or run the cell phone, the voltage between the anode and the cathode (V_{cell}) will always be lower than E_{cell} because of polarization effects.

1.5 Pourbaix (Eh – pH) diagram

The Pourbaix diagram is a plot of reduction potential (E or Eh) versus pH . It is constructed by plotting the Nernst equation for half cell reaction pertaining to one metal species. For the zinc-water system shown in Fig. 1.6, the following half-cell reactions are used to construct the Pourbaix diagram³:

- (i) $Zn^{2+} + 2e = Zn$, (ii) $Zn(OH)_2 + 2H^+ + 2e = Zn + 2H_2O$, (iii) $HZnO_2^- + 3H^+ + 2e = Zn + 2H_2O$
 (iv) $ZnO_2^{2-} + 4H^+ + 2e = Zn + 2H_2O$, (v) $Zn(OH)_2 + 2H^+ = Zn^{2+} + 2H_2O$,
 (vi) $Zn(OH)_2 = HZnO_2^- + H^+$, (vii) $HZnO_2^- = ZnO_2^{2-} + H^+$

The O_2 and H_2 evolution half-cell reactions are superimposed on the Pourbaix diagram.

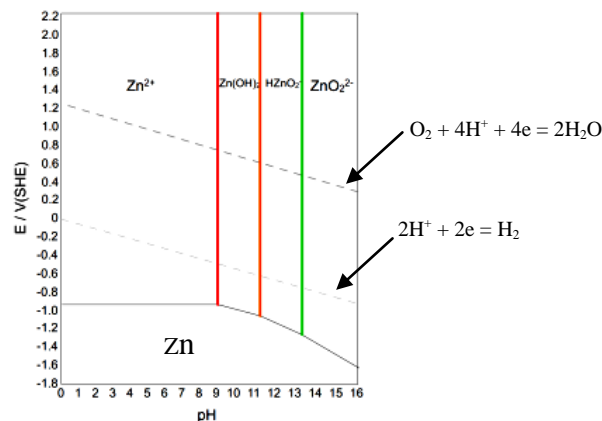


Fig. 1.6. Pourbaix diagram for the Zn-H₂O system³.

Horizontal lines correspond to half-cell reactions that only involve reduction of metal species, as in reaction (i). Slanted lines correspond to half-cell reactions that involve both reduction of metal species and H^+ , as in reactions (ii) to (iv). Vertical lines represent chemical reactions, as in reaction (v) to (vii).

A Pourbaix diagram tells you the possible half-cell reactions as a function of pH. At $pH = 3$ and 15 , the thermodynamically feasible half cell reactions are $Zn^{2+} + 2e = Zn$ and $ZnO_2^{2-} + 4H^+ + 2e = Zn + 2H_2O$ respectively.

³ http://www.doitpoms.ac.uk/tlplib/pourbaix/pourbaix_construction.php

1.6 Example problems

In all worked example, unless it is specifically mentioned, the potentials are with respect to the standard hydrogen electrode (SHE).

Example 1-1

Consider the electrochemical cell: $Zn|Zn^{2+}||Cu^{2+}|Cu$. The zinc and copper solutions are both produced by dissolving the appropriate sulfates. The concentration of zinc sulfate in the left half-cell is 0.005 mol/l and the concentration of copper sulfate in the right half-cell is 0.002 mol/l. Each cell contains 0.005 mol/l H_2SO_4 . Calculate the electrochemical potential of this cell at 298 K using the Debye-Huckel theory. Given $E^\circ(Zn^{2+}/Zn) = -0.76$ V and $E^\circ(Cu^{2+}/Cu) = 0.34$ V.

The cell reaction is: $Zn + Cu^{2+} = Zn^{2+} + Cu$ with $E^\circ_{cell} = 1.10$ V.

Assume 1 dm³ (1 litre) of both anolyte and catholyte. Square and curly brackets denote concentration and activity respectively.

Given: Anolyte: $[Zn^{2+}] = 0.005$ M, $[H^+] = 0.01$, $[SO_4^{2-}] = 0.01$ M
Catholyte: $[Cu^{2+}] = 0.002$ M, $[H^+] = 0.01$, $[SO_4^{2-}] = 0.007$ M

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{2} \log \frac{\{Zn^{2+}\}}{\{Cu^{2+}\}} \quad (e1-1.1)$$

$$\{Zn^{2+}\} = \gamma_{\pm, ZnSO_4} [Zn^{2+}] \quad (e1-1.2)$$

$$\{Cu^{2+}\} = \gamma_{\pm, CuSO_4} [Cu^{2+}] \quad (e1-1.3)$$

Anolyte

$$I = 0.5 \sum_{i=1}^2 C_i z_i^2 = 0.5[Zn^{2+}](+2)^2 + 0.5[H^+](+1)^2 + 0.5[SO_4^{2-}](-2)^2 = 0.035 \text{ M} \quad (e1-1.4)$$

Using extended Debye-Huckel law, that is,

$$\log(\gamma_{\pm, ZnSO_4}) = \frac{-A|z_+z_-|I^{0.5}}{1+I^{0.5}} = \frac{-0.509 \times 4 \times 0.035^{0.5}}{1+0.035^{0.5}} = -0.32 \quad (e1-1.5)$$

$$\gamma_{\pm, ZnSO_4} = 0.48 \quad (e1-1.6)$$

Catholyte

$$I = 0.5 \sum_{i=1}^2 C_i z_i^2 = 0.5[Cu^{2+}](+2)^2 + 0.5[H^+](+1)^2 + 0.5[SO_4^{2-}](-2)^2 = 0.023 \text{ M} \quad (e1-1.7)$$

$$\log(\gamma_{\pm, CuSO_4}) = \frac{-A|z_+z_-|I^{0.5}}{1+I^{0.5}} = \frac{-0.509 \times 4 \times 0.023^{0.5}}{1+0.023^{0.5}} = -0.27 \quad (e1-1.8)$$

$$\gamma_{\pm, CuSO_4} = 0.54 \quad (e1-1.9)$$

From e1-1-2 and e1-1.3,

$$\{Zn^{2+}\} = 0.48 \times 0.005 = 0.0024 \text{ M}, \quad \{Cu^{2+}\} = 0.54 \times 0.002 = 0.0011 \text{ M} \quad (e1-1.10)$$

Substituting e1-1.10 in e1-1.1, we get:

$$E_{cell} = 1.10 - \frac{0.059}{2} \log \frac{0.0024}{0.0011} = 1.09 \text{ V}$$

This problem suggests that you can $E_{cell} = E_{cell}^{\circ}$ to a good approximation in many cases, as ion concentrations do not significantly change E_{cell} .

Example 1-2

A voltaic cell is constructed that uses the following reaction $\text{Ni} + 2\text{Ag}^+ = \text{Ni}^{2+} + 2\text{Ag}$.

a) Write the half reactions & indicate the anodic or cathodic reactions.

b) Calculate E_{cell}°

c) State whether the reaction is spontaneous.

Given: $E^{\circ}(\text{Ni}^{2+}/\text{Ni}) = -0.28\text{V}$, $E^{\circ}(\text{Ag}^+/\text{Ag}) = +0.80\text{V}$

a) The half cell reactions are:



b) Cell reaction: $\text{Ni} + \text{Ag}^+ = \text{Ni}^{2+} + \text{Ag}$ $E_{cell}^{\circ} = E'_{a} + E'_{c} = 1.08 \text{ V}$

c) $\Delta G_{cell}^{\circ} = -nFE_{cell}^{\circ} = -2 \times 96500 \times 1.1 = -212 \text{ kJ}$. Hence the cell reaction is spontaneous.

Example 1-3

Calculate the potential of a silver wire, with respect to SCE, immersed in a 1.0 mM AgNO_3 solution. Ignore activity coefficients. The potential of SCE with respect to the SHE is +0.242 V.

The relevant reaction is $\text{Ag}^+ + \text{e} = \text{Ag}$, $E^{\circ}(\text{Ag}^+/\text{Ag}) = 0.80 \text{ V}$, $[\text{Ag}^+] = 0.001 \text{ M}$.

$$E(\text{Ag}^+/\text{Ag})_{SHE} = 0.8 - \frac{0.059}{2} \log \frac{1}{[0.001]} = 0.71 \text{ V}$$

$$\therefore E(\text{Ag}^+/\text{Ag})_{SCE} = E(\text{Ag}^+/\text{Ag})_{SHE} - E^{\circ}(SCE) = 0.71 - 0.242 = 0.47 \text{ V}$$

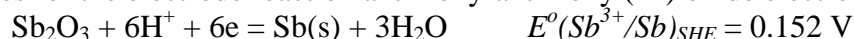
To ensure that you do not make any mistakes in converting from SHE scale to SCE scale, please do the following:

- (i) Mark $E(\text{Ag}^+/\text{Ag}) = 0.71 \text{ V}$, $E^{\circ}(SCE) = 0.242 \text{ V}$, and $E^{\circ}(\text{H}^+/\text{H}_2) = 0$ on the right side of a vertical line. This line is the SHE scale.
- (ii) In a SCE scale, $E^{\circ}(SCE) = 0$. Hence convert all values from SHE scale to SCE scale by subtracting 0.242 V from them. Write these values on the left hand side of the line.
- (iii) The value next to $E(\text{Ag}^+/\text{Ag})$ on the left hand side of the line is $E(\text{Ag}^+/\text{Ag})_{SCE}$

Learning: Example 1-3 shows an electrochemical technique for determining ion concentration in solution by measuring half-cell potential.

Example 1-4

The following equation applies for the electrode reaction antimony-antimony (III) oxide electrode:



Calculate the pH of a solution, which gives rise to a potential of -0.718 V vs. SCE on such an electrode.

First convert -0.718 V from SCE scale to SHE scale. Therefore,

$$E(\text{Sb}^{3+}/\text{Sb})_{\text{SCE}} = E(\text{Sb}^{3+}/\text{Sb})_{\text{SHE}} - E^{\circ}(\text{SCE})$$

or,
$$E(\text{Sb}^{3+}/\text{Sb})_{\text{SHE}} = -0.718 + 0.242 = -0.476 \text{ V}$$

Now,
$$E(\text{Sb}^{3+}/\text{Sb})_{\text{SHE}} = E^{\circ}(\text{Sb}^{3+}/\text{Sb})_{\text{SHE}} - \frac{0.059}{6} \log \frac{1}{\{\text{H}^+\}^6}$$

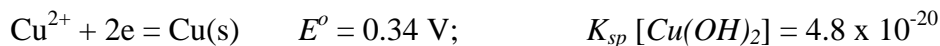
or,
$$-0.476 = 0.152 - 0.059 \text{ pH}$$

or,
$$\text{pH} = 10.5$$

Learning: Example 1-4 shows an electrochemical technique for determining pH of a solution by measuring cell potential.

Example 1-5

A novel pH sensitive electrode can be constructed by anodizing a copper wire, which oxidizes to Cu^{+2} in a solution containing OH^- , resulting in the formation of an insoluble $\text{Cu}(\text{OH})_2$ coating on the wire. A basic solution yields a potential of -0.254 V vs. SCE with this electrode. Calculate the pH of the solution. The relevant equilibria are:



Unlike example 1-4, pH does not come directly from the given half-cell reaction, but from the solubility product.

$$E(\text{Cu}^{2+}/\text{Cu})_{\text{SCE}} = E(\text{Cu}^{2+}/\text{Cu})_{\text{SHE}} - E^{\circ}(\text{SCE})$$

$$E(\text{Cu}^{2+}/\text{Cu})_{\text{SHE}} = -0.254 + 0.242 = -0.012 \text{ V}$$

$$E(\text{Cu}^{2+}/\text{Cu})_{\text{SHE}} = E^{\circ}(\text{Cu}^{2+}/\text{Cu})_{\text{SHE}} - \frac{0.059}{2} \log \left\{ \frac{1}{\{\text{Cu}^{2+}\}} \right\} \quad (\text{e1-5.1})$$

or,
$$-0.012 = 0.34 + 0.03 \log \{\text{Cu}^{2+}\}$$

\therefore
$$\{\text{Cu}^{2+}\} = 1.85 \times 10^{-12} \text{ M}$$

Now,
$$K_{\text{sp}} = \{\text{Cu}^{2+}\} \{\text{OH}^{-2}\}^2 = \{\text{Cu}^{2+}\} \times \frac{10^{-28}}{\{\text{H}^+\}^2} = 4.8 \times 10^{-20}$$

$$\{\text{H}^+\} = 6.2 \times 10^{-11}$$

Hence
$$\text{pH} = -\log \{\text{H}^+\} = 10.2$$

Please note that even though in reality the copper is being oxidized, that is, $\text{Cu}(\text{s}) = \text{Cu}^{2+} + 2\text{e}$ reaction is taking place, we have considered the reduction reaction $\text{Cu}^{2+} + 2\text{e} = \text{Cu}(\text{s})$. You can check that even if consider the $\text{Cu} = \text{Cu}^{2+} + 2\text{e}$, e1-5.1 and hence $\{\text{Cu}^{2+}\}$ will remain unchanged.

Example 1-6

The solubility product of AgBr(s) is determined in the following manner. A silver cathode is suspended in a saturated solution of AgBr. This half-cell is connected by a salt bridge to a standard hydrogen electrode, which is the anode. The potential of this galvanic cell is + 0.44 volt. Calculate the K_{sp} of AgBr. Given $E^{\circ}(Ag^{+}/Ag) = 0.8 \text{ V}$

$$K_{sp}(\text{AgBr}) = \{Ag^{+}\}\{Br^{-}\}$$

From the dissolution reaction, $\text{AgBr}(s) = Ag^{+} + Br^{-}$, we conclude that, at equilibrium,

$$\{Br^{-}\} = \{Ag^{+}\}$$

$$\therefore K_{sp}(\text{AgBr}) = \{Ag^{+}\}^2 \quad (\text{e1-6.1})$$

$\{Ag^{+}\}$ can be calculated from the potential of the half cell reaction $Ag^{+} + e = Ag$, $E(Ag^{+}/Ag) = 0.44\text{V}$.

$$E(Ag^{+}/Ag) = E^{\circ}(Ag^{+}/Ag) - \frac{0.059}{1} \log \left\{ \frac{1}{\{Ag^{+}\}} \right\}$$

$$\text{or,} \quad \{Ag^{+}\} = 10^{-6}M \quad (\text{e1-6.2})$$

Substituting e1-6.2 in e1-6.1, we get, $K_{sp}(\text{AgBr}) = 10^{-12}$