17.10: Electromotive Force of Galvanic Cells

Using a voltmeter to measure the **electrical potential difference** (commonly called voltage) between two electrodes provides a quantitative indication of just how spontaneous a redox reaction is. The potential difference is measured in **volts** (V), an SI unit which corresponds to one joule per ampere-second (1V = 1 J A^{-1} s^{-1}). The voltage indicates the tendency for current to flow in the external circuit, that is, it shows how strongly the anode reaction can push electrons into the circuit and how strongly the cathode reaction can pull them out. The potential difference is greatest when a large electrical resistance in the external circuit prevents any current from flowing. The maximum potential difference which can be measured for a given cell is called the **electromotive force**, abbreviated emf and represented by the symbol *E*.

By convention, when a cell is written in shorthand notation, its *emf is given a positive value if the cell reaction is spontaneous*. That is, if the electrode on the left forces electrons into the external circuit and the electrode on the right withdraws them, then the dial on the voltmeter gives the cell emf. On the other hand, if the half-cell on the right side of the shorthand cell notation is releasing electrons, making the right-hand terminal of the voltmeter negative, the cell emf is minus the reading of the meter. This corresponds to a nonspontaneous cell reaction, written in the conventional way.

Example 17.10.1 : Galvanic Cell EMF

When the galvanic cell shown in Figure 2 from Galvanic Cells is connected to a voltmeter, the reading is 0.59 V. The shorthand notation for this cell is

$$\mathrm{Pt, Cl_2(g) \mid Cl^-(1\,M) \parallel Fe^{2+}(1\,M), Fe^{3+}(1\,M)|Pt}$$

What is the value of the cell emf?

Solution:

We have already seen that this cell as written corresponds to a nonspontaneous reaction. Therefore the emf must be negative and *E* = – 0.59 V.

Example 17.10.2 : Voltmeter Readings

If the voltmeter in Figure 17.5 reads 1.10 V, what is the emf for the cell

$$\mathrm{Cu|Cu^{2+}(1\,M) \parallel Zn^{2+}(1\,M)|Zn}$$

Solution

In this case the shorthand notation corresponds to the reverse of Eq. (1) in Galvanic Cells; that is, it refers to the nonspontaneous cell reaction

$$\mathrm{Cu + Zn^{2+} \rightarrow Cu^{2+} + Zn}$$

Consequently the emf for this cell must be negative and E = –1.10 V.

Example $17.10.2$ shows that if the cell notation is written in reverse, the cell emf changes sign, since for the spontaneous reaction shown in Eq. (2) from Galvanic Cells the emf would have been +1.10 V.

Experimentally measured cell emf's are found to depend on the concentrations of species in solution and on the pressures of gases involved in the cell reaction. Consequently it is necessary to specify concentrations and pressures when reporting an emf, and we shall only consider cells in which all concentrations are 1mol dm^{-3} and all pressures are 1 atm (101.3 kPa).

The emf of such a cell is said to be its **standard electromotive force** and is given the symbol *E*°.

The electromotive forces of galvanic cells are found to be additive. That is, if we measure the emf’s of the two cells

$$\mathrm{Zn|Z^{2+}(1\,M) \parallel H^+(1\,M) \mid H_2(1\,atm), Pt} \tag{17.10.1}$$

E° = 0.76 V

$$\mathrm{Pt, H_2(1\,atm) \mid H^+(1\,M) \parallel Cu^{2+}(1\,M)|Cu} \tag{17.10.2}$$

$E°$ = 0.34 V

the sum of the $E°$ values corresponds to the measured emf for a third cell with which we discuss in the section on Cell Notation and Conventions:

$$\mathrm{Zn}|\mathrm{Zn}^{2+}(1\,\mathrm{M})\,||\,\mathrm{Cu}^{2+}(1\,\mathrm{M})\,|\,\mathrm{Cu}\mathrm{E}^{o}{=}1\cdot 10 \tag{17.10.3}$$

Whenever the right-hand electrode of one cell is identical to the left-hand electrode of another, we can add the emf's in this way, canceling the electrode which appears twice. This additivity makes it possible to store a large amount of emf data in a small table. By convention such data are tabulated as **standard reduction potentials**. These refer to the emf of a cell whose left-hand electrode is the hydrogen-gas electrode and whose right-hand electrode is the electrode whose emf is being sought. Table 17.10.1contains a number of useful standard reduction potentials.

As an example of the use of the table, the entry corresponding to the electrode $Cu^{2+}(1M)\mid Cu is + 0.34V$. Thus when this electrode is written

TABLE 17.10.1: Standard Reduction Potentials at 298.15 K.

Acidic Solution	**Standard Reduction Potential, $E°$ (volts)**
$\mathrm{F_2(g)} + 2e^{-}/\mathrm{rightarrow}2\,\mathrm{F^{-}(aq)}$	2.87
$\mathrm{Co^{3+}(aq)} + e^{-}/\mathrm{rightarrow}\mathrm{Co^{2+}(aq)}$	1.92
$\mathrm{Au^{+}(aq)} + e^{-} \rightarrow \mathrm{Au(s)}$	1.83
$\mathrm{H_2O_2(aq)} + 2\,\mathrm{H_3O^{+}(aq)} + 2e^{-} \rightarrow 4\,\mathrm{H_2O(l)}$	1.763
$\mathrm{Ce^{4+}(aq)} + e^{-} \rightarrow \mathrm{Ce^{3+}(aq)}$	1.72
$\mathrm{Pb^{4+}(aq)} + 2e^{-} \rightarrow \mathrm{Pb^{2+}(aq)}$	1.69
$\mathrm{PbO_2(s)} + \mathrm{SO_4^{2-}(aq)} + 4\,\mathrm{H_3O^{+}(aq)} + 2e^{-} \rightarrow \mathrm{PbSO_4(s)} + 6\,\mathrm{H_2O(l)}$	1.690
$\mathrm{NiO_2(s)} + 4\,\mathrm{H_3O^{+}(aq)} + 2e^{-} \rightarrow \mathrm{Ni^{2+}(aq)} + 6\,\mathrm{H_2O(l)}$	1.68
$2\,\mathrm{HClO(aq)} + 2\,\mathrm{H3\ O + (aq)} + 2e^{-} \rightarrow \mathrm{Cl_2(g)} + 4\,\mathrm{H_2O(l)}$	1.63
$\mathrm{Au^{3+}(aq)} + 3e^{-} \rightarrow \mathrm{Au(s)}$	1.52
$\mathrm{MnO_4^{-}(aq)} + 8\,\mathrm{H_3O^{+}(aq)} + 5e^{-} \rightarrow \mathrm{Mn^{2+}(aq)} + 12\,\mathrm{H_2O(l)}$	1.51
$\mathrm{BrO_3^{-}(aq)} + 6\,\mathrm{H_3O^{+}(aq)} + 5e^{-} \rightarrow \frac{1}{2}\mathrm{Br_2(aq)} + 9\,\mathrm{H_2O(l)}$	1.478
$2\,\mathrm{ClO_3^{-}(aq)} + 12\,\mathrm{H_3O^{+}(aq)} + 10e^{-} \rightarrow \mathrm{Cl_2(g)} + 18\,\mathrm{H_2O(l)}$	1.47
$\mathrm{Cr_2O_7^{2-}(aq)} + 14\,\mathrm{H_3O^{+}(aq)} + 6e^{-} \rightarrow 2\,\mathrm{Cr^{3+}(aq)} + 21\,\mathrm{H_2O(l)}$	1.36
$\mathrm{Cl_2(g)} + 2e^{-} \rightarrow 2\,\mathrm{Cl^{-}(aq)}$	1.358
$\mathrm{N_2H_5^{+}(aq)} + 3\,\mathrm{H_3O^{+}(aq)} + 2e^{-} \rightarrow 2\,\mathrm{NH_4^{+}(aq)} + 3\,\mathrm{H_2O(l)}$	1.275
$\mathrm{MnO_2(s)} + 4\,\mathrm{H_3O^{+}(aq)} + 2e^{-} \rightarrow \mathrm{Mn^{2+}(aq)} + 6\,\mathrm{H_2O(l)}$	1.23
$\mathrm{O_2(g)} + 4\,\mathrm{H_3O^{+}(aq)} + 4e^{-} \rightarrow 6\,\mathrm{H_2O(l)}$	1.229
$\mathrm{ClO_4^{-}(aq)} + 2\,\mathrm{H_3O^{+}(aq)} + 2e^{-} \rightarrow \mathrm{ClO_3^{-}(aq)} + 3\,\mathrm{H_2O(l)}$	1.201
$\mathrm{IO_3^{-}(aq)} + 6\,\mathrm{H_3O^{+}(aq)} + 5e^{-} \rightarrow \frac{1}{2}\mathrm{I_2(aq)} + 9\,\mathrm{H_2O(l)}$	1.195
$\mathrm{Pt^{2+}(aq)} + 2e^{-} \rightarrow \mathrm{Pt(s)}$	1.188
$\mathrm{Br_2(l)} + 2e^{-} \rightarrow 2\,\mathrm{Br^{-}(aq)}$	1.066
$\mathrm{AuCl_4^{-}(aq)} + 3e^{-} \rightarrow \mathrm{Au(s)} + 4\,\mathrm{Cl^{-}(aq)}$	1.00
$\mathrm{NO_3^{-}(aq)} + 4\,\mathrm{H_3O^{+}(aq)} + 3e^{-} \rightarrow \mathrm{NO(g)} + 6\,\mathrm{H_2O(l)}$	0.96
$\mathrm{NO_3^{-}(aq)} + 3\,\mathrm{H_3O^{+}(aq)} + 2e^{-} \rightarrow \mathrm{HNO_2(aq)} + 4\,\mathrm{H_2O(l)}$	0.94
$\mathrm{Pd^{2+}(aq)} + 2e^{-} \rightarrow \mathrm{Pd(s)}$	0.915
$2\,\mathrm{Hg^{2+}(aq)} + 2e^{-} \rightarrow \mathrm{Hg_2^{2+}(aq)}$	0.9110

Acidic Solution	Standard Reduction Potential, $E°$ (volts)
$Hg^{2+}(aq) + 2e^- \rightarrow Hg(l)$	0.8535
$SbCl_6^-(aq) + 2e^- \rightarrow SbCl_4^-(aq) + 2\,Cl^-(aq)$	0.84
$Ag^+(aq) + e^- \rightarrow Ag(s)$	0.7991
$Hg_2^{2+}(aq) + 2e^- \rightarrow 2\,Hg(l)$	0.7960
$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$	0.771
$[PtCl_4]^{2-}(aq) + 2e^- \rightarrow Pt(s) + 4\,Cl^-(aq)$	0.758
$[PtCl_6]^{2-}(aq) + 2e^- \rightarrow [PtCl_4]^{2-}(aq) + 2\,Cl^-(aq)$	0.726
$O_2(g) + 2\,H_3O^+(aq) + 2e^- \rightarrow H_2O_2(aq) + 2\,H_2O(l)$	0.695
$TeO_2(s) + 4\,H_3O^+(aq) + 4e^- \rightarrow Te(s) + 6\,H_2O(l)$	0.604
$H_3AsO_4(aq) + 2\,H_3O^+(aq) + 2e^- \rightarrow HAsO_2(aq) + 4\,H_2O(l)$	0.560
$I_2(s) + 2e^- \rightarrow 2\,I^-(aq)$	0.535
$Cu^+(aq) + e^- \rightarrow Cu(s)$	0.521
$[RhCl_6]^{3-}(aq) + 3e^- \rightarrow Rh(s) + 6\,Cl^-(aq)$	0.5
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$	0.340
$Hg_2Cl_2(s) + 2e^- \rightarrow 2\,Hg(l) + 2\,Cl^-(aq)$	0.27
$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-(aq)$	0.222
$Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$	0.159
$SO_4^{2-}(aq) + 4\,H_3O^+(aq) + 2e^- \rightarrow H_2SO_3(aq) + 5\,H_2O(l)$	0.158
$Sn^{4+}(aq) + 2e^- \rightarrow Sn^{2+}(aq)$	0.15
$S(s) + 2\,H_3O^+(aq) + 2e^- \rightarrow H_2S(aq) + 2\,H_2O(l)$	0.144
$AgBr(s) + e^- \rightarrow Ag(s) + Br^-(aq)$	0.0713
$2\,H_3O^+(aq) + 2e^- \rightarrow 2\,H_2(g) + 2\,H_2O(l)$ (reference electrode)	0.0000
$N_2O(g) + 6\,H_3O^+(aq) + 4e^- \rightarrow 2\,NH_3OH^+(aq) + 5\,H_2O(l)$	−0.05
$HgS(s, black) + 2\,H_3O^+(aq) + 2e^- \rightarrow Hg(l) + H_2S(g) + 2\,H_2O(l)$	−0.085
$Se(s) + 2\,H_3O^+(aq) + 2e^- \rightarrow H_2Se(aq) + 2\,H_2O(l)$	−0.115
$Pb^{2+}(aq) + 2e^- \rightarrow Pb(s)$	−0.125
$Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)$	−0.1375
$AgI(s) + e^- \rightarrow Ag(s) + I^-(aq)$	−0.1522
$[SnF_6]^{2-}(aq) + 4e^- \rightarrow Sn(s) + 6\,F^-(aq)$	−0.200
$Ni^{2+}(aq) + 2e^- \rightarrow Ni(s)$	−0.25
$Co^{2+}(aq) + 2e^- \rightarrow Co(s)$	−0.277
$Tl^+(aq) + e^- \rightarrow Tl(s)$	−0.3363
$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}(aq)$	−0.3505
$Cd^{2+}(aq) + 2e^- \rightarrow Cd(s)$	−0.403
$Cr^{3+}(aq) + e^- \rightarrow Cr^{2+}(aq)$	−0.424
$Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$	−0.44
$2\,CO_2(g) + 2\,H_3O^+(aq) + 2e^- \rightarrow (COOH)_2(aq) + 2\,H_2O(l)$	−0.481

Acidic Solution	Standard Reduction Potential, $E°$ (volts)
$Ga^{3+}(aq) + 3e^- \rightarrow Ga(s)$	-0.53
$Cr^{3+}(aq) + 3e^- \rightarrow Cr(s)$	-0.74
$Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)$	-0.763
$Cr^{2+}(aq) + 2e^- \rightarrow Cr(s)$	-0.90
$V^{2+}(aq) + 2e^- \rightarrow V(s)$	-1.13
$Mn^{2+}(aq) + 2e^- \rightarrow Mn(s)$	-1.18
$Zr^{4+}(aq) + 4e^- \rightarrow Zr(s)$	-1.55
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	-1.676
$H_2(g) + 2e^- \rightarrow 2\,H^-(aq)$	-2.25
$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$	-2.356
$Na^+(aq) + e^- \rightarrow Na(s)$	-2.714
$Ca^{2+}(aq) + 2e^- \rightarrow Ca(s)$	-2.84
$Sr^{2+}(aq) + 2e^- \rightarrow Sr(s)$	-2.89
$Ba^{2+}(aq) + 2e^- \rightarrow Ba(s)$	-2.92
$Rb^+(aq) + e^- \rightarrow Rb(s)$	-2.925
$K^+(aq) + e^- \rightarrow K(s)$	-2.925
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.045

Basic Solution	Standard Reduction Potential, $E°$ (volts)
$ClO^-(aq) + H_2O(l) + 2e^- \rightarrow Cl^-(aq) + 2\,OH^-(aq)$	0.89
$OOH^-(aq) + H_2O(l) + 2e^- \rightarrow 3\,OH^-(aq)$	0.867
$2\,NH_2OH(aq) + 2e^- \rightarrow N_2H_4(aq) + 2\,OH^-(aq)$	0.73
$ClO_3^-(aq) + 3\,H_2O(l) + 6e^- \rightarrow Cl^-(aq) + 6\,OH^-(aq)$	0.622
$ClO_3^-(aq) + 3\,H_2O(l) + 6e^- \rightarrow Cl^-(aq) + 6\,OH^-(aq)$	0.622
$MnO_4^-(aq) + 2\,H_2O(l) + 3e^- \rightarrow MnO_2(s) + 4\,OH^-(aq)$	0.60
$MnO_4^-(aq) + e^- \rightarrow MnO_4^{2-}(aq)$	0.56
$NiO_2(s) + 2\,H_2O(l) + 2e^- \rightarrow Ni(OH)_2(s) + 2\,OH^-(aq)$	0.49
$Ag_2CrO_4^-(s) + 2e^- \rightarrow 2\,Ag(s) + CrO_4^{2-}(aq)$	0.4491
$O_2(g) + 2\,H_2O(l) + 4e^- \rightarrow 4\,OH^-(aq)$	0.401
$ClO_4^-(aq) + H_2O(l) + 2e^- \rightarrow ClO_3^-(aq) + 2\,OH^-(aq)$	0.374
$Ag_2O(s) + H_2O(l) + 2e^- \rightarrow 2\,Ag(s) + 2\,OH^-(aq)$	0.342
$2\,NO_2^-(aq) + 3\,H_2O(l) + 4e^- \rightarrow N_2O(g) + 6\,OH^-(aq)$	0.15
$[Co(NH_3)_6]^{3+}(aq) + e^- \rightarrow [Co(NH_3)_6]^{3+}(aq)$	0.058
$HgO(s) + H_2O(l) + 2e^- \rightarrow Hg(l) + 2\,OH^-(aq)$	0.0977
$O_2(g) + H_2O(l) + 2e^- \rightarrow OOH^-(aq) + OH^-(aq)$	0.0649
$NO_3^-(aq) + H_2O(l) + 2e^- \rightarrow NO_2^-(aq) + 2\,OH^-(aq)$	0.01
$MnO_2(s) + 2\,H_2O(l) + 2e^- \rightarrow Mn(OH)_2(s) + 2\,OH^-(aq)$	-0.05
$CrO_4^{2-}(aq) + 4\,H_2O(l) + 3e^- \rightarrow Cr(OH)_3(s) + 5\,OH^-(aq)$	-0.11

$Cu_2O(s) + H_2O(l) + 2e^- \rightarrow 2\,Cu(s) + 2\,OH^-(aq)$	-0.365
$FeO_2(aq) + H_2O(l) + 2e^- \rightarrow HFeO_2^-(aq) + OH^-(aq)$	-0.69
$2\,H_2O(l) + 2e^- \rightarrow H_2(g) + 2\,OH^-(aq)$	-0.8277
$2\,NO_3^-(aq) + 2\,H_2O(l) + 2e^- \rightarrow N_2O_4(g) + 4\,OH^-(aq)$	-0.86
$HFeO_2^-(aq) + 2e^- \rightarrow Fe(s) + 3\,OH^-(aq)$	-0.8
$SO_4^{2-}(aq) + H_2O(l) + 2e^- \rightarrow SO_3^{2-}(aq) + 2\,OH^-(aq)$	-0.936
$N_2(g) + 4\,H_2O(l) + 4e^- \rightarrow N_2H_4(aq) + 4\,OH^-(aq)$	-1.16
$[Zn(OH)_4]^{2-}(aq) + 2e^- \rightarrow Zn(s) + 4\,OH^-(aq)$	-1.285
$Zn(OH)_2(s) + 2e^- \rightarrow Zn(s) + 2\,OH^-(aq)$	-1.246
$[Zn(CN)_4]^{2-}(aq) + 2e^- \rightarrow Zn(s) + 4\,CN^-(aq)$	-1.34
$Cr(OH)_3(s) + 3e^- \rightarrow Cr(s) + 3\,OH^-(aq)$	-1.33
$SiO_3^{2-}(aq) + 3\,H_2O(l) + 4e^- \rightarrow Si(s) + 6\,OH^-(aq)$	-1.69

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to the right of Pt, H_2(1 atm) | H^+(1 *M*), as in Eq. 17.10.2above, the *E*° is + 0.34 V. For the Zn^{2+} | Zn redox couple, we find *E*° = – 0.76 V in Table 17.1. This means that for the cell

$$\mathrm{Pt, H_2(1\,atm)\mid H^+(1\,M)\parallel Zn^{2+}(1\,M)\mid Zn E^o{=}{-}0\cdot 76\,V}$$

Since Eq. 17.10.1 shows this cell in reverse, we change the sign of *E*°, obtaining + 0.76 V. Thus we can combine standard reduction potentials from Table 1 to obtain emf's for cells like Eq. 17.10.3so long as both electrodes are given in the table.

Example 17.10.3 : Find the standard emf for the cell

$$\mathrm{Hg(l)\mid Hg^{2+}(1\,M)\parallel Br^-\mid Br_2(l), Pt}$$

Solution

From Table 17.10.1we have;

$$\mathrm{Pt, H_2(1\,atm)\mid H^+(1\,M)\parallel Hg^{2+}(1\,M)\mid Hg(l) E^o{=}{+}0\cdot 85\,V}$$

Since we want to be the left-hand electrode, this must be reversed and the sign of *E*° must be changed:

$$\mathrm{Hg(l)\mid Hg^{2+}(1\,M)\parallel H^+(1\,M)\mid} H_2(1atm), PtE^o = -0.85V \tag{17.10.4}$$

For the other electrode Table 17.10.1gives

$$\mathrm{Pt, H_2(1\,atm)\mid H^+(1\,M)\parallel Br^-(1\,M)\mid Br_2(l), PtE^o{=}{+}1\cdot 07\,V} \tag{17.10.5}$$

Adding the cells of Eqs. 17.10.4and 17.10.5, we obtain

$$\mathrm{Hg(l)\mid Hg^{2+}(1\,M)\parallel Br^-(1\,M)\mid Br_2(l), PtE^o{=}(1\cdot 07-0\cdot 85\,)V{=}{+}0\cdot 22\,V}$$

The positive value of the standard emf obtained in Example 17.10.3indicates that the corresponding cell reaction is spontaneous:

$$\mathrm{Hg(l) + Br_2(l) \rightarrow Hg^{2+}(1\,M) + 2\,Br^-(1\,M)}$$

In other words, bromine is a strong enough oxidizing agent to convert mercury metal to mercury(II) ions in aqueous solution, assuming the concentrations of mercury(II) and bromide ions to be 1 mol dm^{-3}. This corresponds to the observations made where liquid mercury combined with liquid bromine to form mercury(II) bromide. Thus the standard reduction potentials in Table 17.10.1 can be used to predict whether a particular reaction will take place, just as Table 1 in Redox Couples was used in our earlier discussion of redox reactions. The advantage of Table 17.10.1is that it gives quantitative as well as qualitative information. It not only tells us that $Br_2(l)$ is a stronger oxidizing agent than Hg^{2+} (1 *M*) [because $Br_2(l)$ is above Hg^{2+} (1 *M*), but it also tells us how much stronger, in terms of the cell emf of + 0.22 V.