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Electrochemistry introduction



In electrochemistry, a potential difference between two half-cells is set up by having different redox couples and/or different concentrations of a given redox couple present.

Part A Introduction

| The potential of the | side half-cell is measured relative to the | side one, |
|----------------------------------|---|-------------------------|
| so the cell potential is given b | y subtracting the reduction potential of the | side from |
| the reduction potential of the | side. Standard reduction potent | tials can be tabulated, |
| which correspond to values re | ecorded under standard conditions against | the standard |
| electrode. The co | nventional cell reaction consists of the right | -hand side |
| and the left-hand side | (which can be thought of as subtractin | g the left-hand side |
|), making sure that | \overline{t} the number of electrons (n) transferred is | the same for both |
| sides. | | |
| | | |
| Items: | | |
| right-hand left-hand pla | tinum silver hydrogen oxygen oxid | dation reduction |
| | | |
| | | |

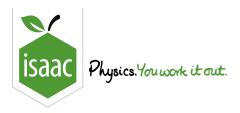
Part B Linking equations

Working out cell potentials can be useful in itself, but as a result of connections to other thermodynamic quantities, tabulated standard reduction potentials allow us to calculate, for example, equilibrium constants even of non-redox reactions or processes such as a salt dissolving.

Given that $\Delta_r G^{\circ} = -nFE^{\circ} = -RT \ln K$, rearrange the equation for K (the equilibrium constant) as a function of n (the number of electrons transferred), F (the Faraday constant), E° (the standard cell potential, for which you should use E^o in your expression), R (the universal gas constant) and T (the temperature).

The following symbols may be useful: E^o, F, K, R, T, e, ln(), log(), n

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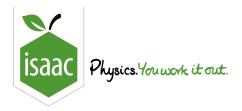
Physical

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| Name the element whose reduction is used as a standard by which all electrode potentials are measured. | | |
|--|----------|--|
| | Helium | |
| | Hydrogen | |
| | Silver | |
| | Lithium | |
| | Iron | |
| | Fluorine | |
| | Platinum | |
| | Oxygen | |
| | | |
| | | |

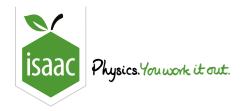


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The standard electrode potential, E° , for the reduction, $\mathrm{Br_2}(\mathrm{aq}) + 2\,\mathrm{e^-} \longrightarrow 2\,\mathrm{Br^-}(\mathrm{aq})$ is $1.09\,\mathrm{V}$. Give the E° value for the reduction, $\frac{1}{2}\mathrm{Br_2}(\mathrm{aq}) + \mathrm{e^-} \longrightarrow \mathrm{Br^-}(\mathrm{aq})$.



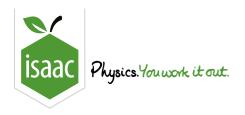
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 E° for the reaction, $\operatorname{Ce}^{4+}(\operatorname{aq}) + \operatorname{e}^{-} \longrightarrow \operatorname{Ce}^{3+}(\operatorname{aq})$ is $1.70\,\mathrm{V}$. Give the E° value for the oxidation half-reaction, $\operatorname{Ce}^{3+}(\operatorname{aq}) \longrightarrow \operatorname{Ce}^{4+}(\operatorname{aq}) + \operatorname{e}^{-}$.



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| Reduction | $E^{\scriptscriptstyle \oplus}$ / $ m V$ |
|--|--|
| $\mathrm{Zn}^{2+}\left(\mathrm{aq} ight)+2\mathrm{e}^{-}\longrightarrow\mathrm{Zn}\left(\mathrm{s} ight)$ | -0.76 |
| $\mathrm{Cr}^{3+}\left(\mathrm{aq} ight)+3\mathrm{e}^{-}\longrightarrow\mathrm{Cr}\left(\mathrm{s} ight)$ | -0.74 |
| $\mathrm{Fe}^{2+}\left(\mathrm{aq} ight)+2\mathrm{e}^{-}\longrightarrow\mathrm{Fe}\left(\mathrm{s} ight)$ | -0.44 |
| $\mathrm{Cu}^{2+}\left(\mathrm{aq} ight) + \mathrm{e}^{-} \longrightarrow \mathrm{Cu}^{+}\left(\mathrm{aq} ight)$ | +0.16 |
| $\mathrm{Cu}^{2+}(\mathrm{aq}) + 2\mathrm{e}^- \longrightarrow \mathrm{Cu}(\mathrm{s})$ | +0.34 |
| $\mathrm{Cu}^{+}\left(\mathrm{aq} ight)+\mathrm{e}^{-}\longrightarrow\mathrm{Cu}\left(\mathrm{s} ight)$ | +0.52 |
| $\mathrm{Fe}^{3+}\left(\mathrm{aq} ight) + \mathrm{e}^{-} \longrightarrow \mathrm{Fe}^{2+}\left(\mathrm{aq} ight)$ | +0.77 |
| $\mathrm{Ag}^{+}\left(\mathrm{aq} ight)+\mathrm{e}^{-}\longrightarrow\mathrm{Ag}\left(\mathrm{s} ight)$ | +0.80 |
| $\mathrm{Cr_2O_7}^{2-}\mathrm{(aq)} + 6\mathrm{e^-} + 14\mathrm{H^+}\mathrm{(aq)} \longrightarrow 2\mathrm{Cr}^{3+}\mathrm{(aq)} + 7\mathrm{H_2O}\mathrm{(l)}$ | +1.33 |

Use the standard electrode potentials tabulated above to calculate the standard cell potentials due to the following reactions:

Part A (a)

$$\operatorname{Zn}\left(s\right) +\operatorname{Cu}^{2+}\left(\operatorname{aq}\right) \longrightarrow\operatorname{Zn}^{2+}\left(\operatorname{aq}\right) +\operatorname{Cu}\left(s\right)$$

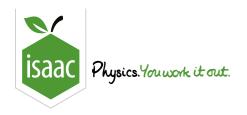
$$Cu\left(s\right)+2\,Ag^{+}\left(aq\right)\longrightarrow Cu^{2+}\left(aq\right)+2\,Ag\left(s\right)$$

Part C (c)

$$6\,\mathrm{Fe}^{2+}\left(aq\right)+\mathrm{Cr}_{2}\mathrm{O_{7}}^{2-}\left(aq\right)+14\,\mathrm{H}^{+}\left(aq\right)\longrightarrow6\,\mathrm{Fe}^{3+}\left(aq\right)+2\,\mathrm{Cr}^{3+}\left(aq\right)+7\,\mathrm{H}_{2}\mathrm{O}\left(l\right)$$

Part D (d)

$$\mathrm{Fe}^{2+}\left(\mathrm{aq}\right)+\mathrm{Zn}\left(\mathrm{s}\right)\longrightarrow\mathrm{Fe}\left(\mathrm{s}\right)+\mathrm{Zn}^{2+}\left(\mathrm{aq}\right)$$



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| Reduction | $E^{\scriptscriptstyle \oplus}$ / $ m V$ |
|--|--|
| $\mathrm{Zn}^{2+}\left(\mathrm{aq} ight)+2\mathrm{e}^{-}\longrightarrow\mathrm{Zn}\left(\mathrm{s} ight)$ | -0.76 |
| $\mathrm{Cr}^{3+}\left(\mathrm{aq} ight)+3\mathrm{e}^{-}\longrightarrow\mathrm{Cr}\left(\mathrm{s} ight)$ | -0.74 |
| $\mathrm{Fe}^{2+}\left(\mathrm{aq} ight)+2\mathrm{e}^{-}\longrightarrow\mathrm{Fe}\left(\mathrm{s} ight)$ | -0.44 |
| $\mathrm{Cu}^{2+}\left(\mathrm{aq} ight) + \mathrm{e}^{-} \longrightarrow \mathrm{Cu}^{+}\left(\mathrm{aq} ight)$ | +0.16 |
| $\mathrm{Cu}^{2+}(\mathrm{aq}) + 2\mathrm{e}^- \longrightarrow \mathrm{Cu}(\mathrm{s})$ | +0.34 |
| $\mathrm{Cu}^{+}\left(\mathrm{aq} ight)+\mathrm{e}^{-}\longrightarrow\mathrm{Cu}\left(\mathrm{s} ight)$ | +0.52 |
| $\mathrm{Fe}^{3+}\left(\mathrm{aq} ight) + \mathrm{e}^{-} \longrightarrow \mathrm{Fe}^{2+}\left(\mathrm{aq} ight)$ | +0.77 |
| $\mathrm{Ag}^{+}\left(\mathrm{aq} ight)+\mathrm{e}^{-}\longrightarrow\mathrm{Ag}\left(\mathrm{s} ight)$ | +0.80 |
| $\mathrm{Cr_2O_7}^{2-}\mathrm{(aq)} + 6\mathrm{e^-} + 14\mathrm{H^+}\mathrm{(aq)} \longrightarrow 2\mathrm{Cr}^{3+}\mathrm{(aq)} + 7\mathrm{H_2O}\mathrm{(l)}$ | +1.33 |

Using the data tabulated above, calculate the standard electrode potentials for the following reductions:

Part A (a)

$$rac{1}{2}\mathrm{Zn}^{2+}\left(\mathrm{aq}
ight)+\mathrm{e}^{-} \longrightarrow rac{1}{2}\mathrm{Zn}\left(\mathrm{s}
ight)$$

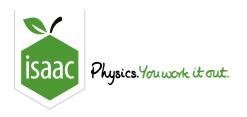
$$\mathrm{Fe}^{3+}\left(\mathrm{aq}\right)+3\,\mathrm{e}^{-}\longrightarrow\mathrm{Fe}\left(\mathrm{s}\right)$$

Part C (c)

$$\mathrm{Cu}^{2+}\left(\mathrm{aq}
ight) + \mathrm{e}^{-} \longrightarrow \mathrm{Cu}^{+}\left(\mathrm{aq}
ight)$$

Part D (d)

$${\rm Cr_2O_7}^{2-}{\rm (aq)} + 14\,{\rm H^+}{\rm (aq)} + 12\,{\rm e^-} \longrightarrow 2\,{\rm Cr}{\rm (s)} + 7\,{\rm H_2O}{\rm (l)}$$



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Chemistry

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Essential Pre-Uni Chemistry L1.7



| Reduction | $E^{\scriptscriptstyle \oplus}$ / $ m V$ |
|--|--|
| $\mathrm{Zn}^{2+}\left(\mathrm{aq} ight)+2\mathrm{e}^{-}\longrightarrow\mathrm{Zn}\left(\mathrm{s} ight)$ | -0.76 |
| $\mathrm{Cr}^{3+}\left(\mathrm{aq} ight)+3\mathrm{e}^{-}\longrightarrow\mathrm{Cr}\left(\mathrm{s} ight)$ | -0.74 |
| $\mathrm{Fe}^{2+}\left(\mathrm{aq} ight)+2\mathrm{e}^{-}\longrightarrow\mathrm{Fe}\left(\mathrm{s} ight)$ | -0.44 |
| $\mathrm{Cu}^{2+}\left(\mathrm{aq} ight) + \mathrm{e}^{-} \longrightarrow \mathrm{Cu}^{+}\left(\mathrm{aq} ight)$ | +0.16 |
| $\mathrm{Cu}^{2+}(\mathrm{aq}) + 2\mathrm{e}^- \longrightarrow \mathrm{Cu}(\mathrm{s})$ | +0.34 |
| $\mathrm{Cu}^{+}\left(\mathrm{aq} ight)+\mathrm{e}^{-}\longrightarrow\mathrm{Cu}\left(\mathrm{s} ight)$ | +0.52 |
| $\mathrm{Fe}^{3+}\left(\mathrm{aq} ight) + \mathrm{e}^{-} \longrightarrow \mathrm{Fe}^{2+}\left(\mathrm{aq} ight)$ | +0.77 |
| $\mathrm{Ag}^{+}\left(\mathrm{aq} ight)+\mathrm{e}^{-}\longrightarrow\mathrm{Ag}\left(\mathrm{s} ight)$ | +0.80 |
| $\mathrm{Cr_2O_7}^{2-}\mathrm{(aq)} + 6\mathrm{e^-} + 14\mathrm{H^+}\mathrm{(aq)} \longrightarrow 2\mathrm{Cr}^{3+}\mathrm{(aq)} + 7\mathrm{H_2O}\mathrm{(l)}$ | +1.33 |

Using the data tabulated above, calculate the standard cell potential for:

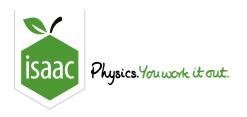
(a) Part A

$$2\operatorname{Cu}^{+}\left(\operatorname{aq}\right) \longrightarrow \operatorname{Cu}\left(\operatorname{s}\right) + \operatorname{Cu}^{2+}\left(\operatorname{aq}\right)$$

$$3\operatorname{Fe}^{2+}\left(\operatorname{aq}\right)\longrightarrow2\operatorname{Fe}^{3+}\left(\operatorname{aq}\right)+\operatorname{Fe}\left(\operatorname{s}\right)$$

Part C (c)

$$Ag^{+}\left(aq\right)+Cu^{+}\left(aq\right)\longrightarrow Ag\left(s\right)+Cu^{2+}\left(aq\right)$$



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Physical

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| Reduction | $E^{\scriptscriptstyle +}$ / $ m V$ |
|--|-------------------------------------|
| $\mathrm{Zn}^{2+}\left(\mathrm{aq} ight)+2\mathrm{e}^{-}\longrightarrow\mathrm{Zn}\left(\mathrm{s} ight)$ | -0.76 |
| $\mathrm{Cr}^{3+}\left(\mathrm{aq} ight)+3\mathrm{e}^{-}\longrightarrow\mathrm{Cr}\left(\mathrm{s} ight)$ | -0.74 |
| $\mathrm{Fe}^{2+}(\mathrm{aq}) + 2\mathrm{e}^- \longrightarrow \mathrm{Fe}(\mathrm{s})$ | -0.44 |
| $\mathrm{Cu}^{2+}\left(\mathrm{aq} ight)+2\mathrm{e}^{-}\longrightarrow\mathrm{Cu}\left(\mathrm{s} ight)$ | +0.34 |
| $\mathrm{Cu}^{+}\left(\mathrm{aq} ight) + \mathrm{e}^{-} \longrightarrow \mathrm{Cu}\left(\mathrm{s} ight)$ | +0.52 |
| $\mathrm{Fe}^{3+}\left(\mathrm{aq} ight) + \mathrm{e}^{-} \longrightarrow \mathrm{Fe}^{2+}\left(\mathrm{aq} ight)$ | +0.77 |
| $\mathrm{Ag}^{+}\left(\mathrm{aq} ight)+\mathrm{e}^{-}\longrightarrow\mathrm{Ag}\left(\mathrm{s} ight)$ | +0.80 |
| ${ m Cr_2O_7}^{2-}({ m aq}) + 6{ m e}^- + 14{ m H}^+({ m aq}) \longrightarrow 2{ m Cr}^{3+}({ m aq}) + 7{ m H_2O}({ m l})$ | +1.33 |

Use the standard electrode potentials tabulated above to find $\Delta G^{\scriptscriptstyle \oplus}$ for the following reactions:

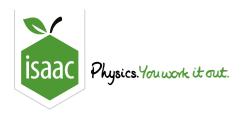
Part A

$$\mathrm{Ag}^{+}(\mathrm{aq}) + \mathrm{e}^{-} \longrightarrow \mathrm{Ag}(\mathrm{s})$$

$$\mathrm{Zn}^{2+}\left(\mathrm{aq}\right)+2\,\mathrm{e}^{-}\longrightarrow\mathrm{Zn}\left(\mathrm{s}\right)$$

Part C (c)

$$\mathrm{Fe}^{3+}(\mathrm{aq}) + 3\,\mathrm{e}^{-} \longrightarrow \mathrm{Fe}(\mathrm{s})$$



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Chemistry

Physical Electrochem

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| Reduction | $E^{\scriptscriptstyle +}$ / $ m V$ |
|--|-------------------------------------|
| $\mathrm{Zn}^{2+}\left(\mathrm{aq} ight)+2\mathrm{e}^{-}\longrightarrow\mathrm{Zn}\left(\mathrm{s} ight)$ | -0.76 |
| $\mathrm{Cr}^{3+}\left(\mathrm{aq} ight)+3\mathrm{e}^{-}\longrightarrow\mathrm{Cr}\left(\mathrm{s} ight)$ | -0.74 |
| $\mathrm{Fe}^{2+}(\mathrm{aq}) + 2\mathrm{e}^- \longrightarrow \mathrm{Fe}(\mathrm{s})$ | -0.44 |
| $\mathrm{Cu}^{2+}\left(\mathrm{aq} ight)+2\mathrm{e}^{-}\longrightarrow\mathrm{Cu}\left(\mathrm{s} ight)$ | +0.34 |
| $\mathrm{Cu}^{+}\left(\mathrm{aq} ight) + \mathrm{e}^{-} \longrightarrow \mathrm{Cu}\left(\mathrm{s} ight)$ | +0.52 |
| $\mathrm{Fe}^{3+}\left(\mathrm{aq} ight) + \mathrm{e}^{-} \longrightarrow \mathrm{Fe}^{2+}\left(\mathrm{aq} ight)$ | +0.77 |
| $\mathrm{Ag}^{+}\left(\mathrm{aq} ight)+\mathrm{e}^{-}\longrightarrow\mathrm{Ag}\left(\mathrm{s} ight)$ | +0.80 |
| ${ m Cr_2O_7}^{2-}({ m aq}) + 6{ m e}^- + 14{ m H}^+({ m aq}) \longrightarrow 2{ m Cr}^{3+}({ m aq}) + 7{ m H_2O}({ m l})$ | +1.33 |

Use the standard electrode potentials tabulated above to find $\Delta G^{\scriptscriptstyle \oplus}$ for the following reactions:

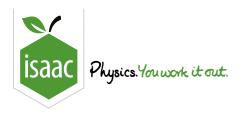
Part A (a)

$$Ag^{+}(aq) + Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + Ag(s)$$
. Give your answer to 1 significant figure.

 $3\,Zn\left(s\right)+Cr_{2}O_{7}^{\,2-}\left(aq\right)+14\,H^{+}\left(aq\right)\longrightarrow3\,Zn^{2+}\left(aq\right)+2\,Cr^{3+}\left(aq\right)+7\,H_{2}O\left(l\right). \label{eq:equation:equ$

Part C (c)

 $2\operatorname{Cr}\left(s\right)+3\operatorname{Cu}^{2+}\left(aq\right)\longrightarrow 2\operatorname{Cr}^{3+}\left(aq\right)+3\operatorname{Cu}\left(s\right).$ Give your answer to 3 significant figures.



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Essential Pre-Uni Chemistry H2.9



The displacement of hydrogen from acid by iron,

$$2 \operatorname{H}^{+}(\operatorname{aq}) + \operatorname{Fe}(\operatorname{s}) \rightleftharpoons \operatorname{Fe}^{2+}(\operatorname{aq}) + \operatorname{H}_{2}(\operatorname{g})$$

has a standard cell potential of $0.44\,V$. Find the associated standard Gibbs free energy change. (Faraday constant = $96\,485\,C\,\mathrm{mol}^{-1}$)