

Introduction

Part A

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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.

The potential of the side half-cell is measured relative to the	side one, so the cell
potential is given by subtracting the reduction potential of the	side from the reduction potential of
the side. Standard reduction potentials can be tabulated, wh	ich correspond to values recorded
under standard conditions against the standard electrode. The	ne conventional cell reaction
consists of the right-hand side and the left-hand side	(which can be thought of as
subtracting the left-hand side ), making sure that the number	of electrons $(n)$ transferred is the
same for both sides.	
Items:	
right-hand     left-hand     platinum     silver     hydrogen     oxygen	dation reduction

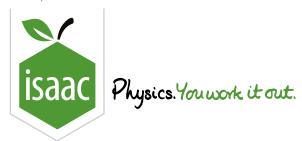
## Part B Linking equations

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),  $E^{\circ}$  (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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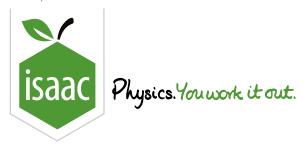


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# Essential Pre-Uni Chemistry L1.1



Name the element whose reduction is used as a standard by which all electrode potentials are measured.	
Helium	
Oxygen	
Silver	
Fluorine	
Platinum	
Lithium	
○ Iron	
Hydrogen	
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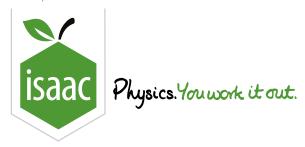
## Essential Pre-Uni Chemistry L1.3



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

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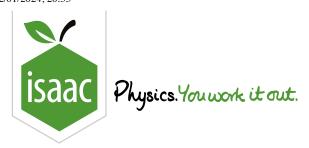
# Essential Pre-Uni Chemistry L1.4



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

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Chemistry

Physical Electrochemistry

Essential Pre-Uni Chemistry L1.5

# Essential Pre-Uni Chemistry L1.5



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
$\mathrm{Fe^{2+}}\left(\mathrm{aq} ight)+2\mathrm{e^{-}}\longrightarrow\mathrm{Fe}\left(\mathrm{s} ight)$	-0.44
$\mathrm{Cu}^{2+}\left(\mathrm{aq} ight) + \mathrm{e}^{-} \longrightarrow \mathrm{Cu}^{+}\left(\mathrm{aq} ight)$	+0.16
$\mathrm{Cu}^{2+}\left(\mathrm{aq} ight)+2\mathrm{e}^{-}\longrightarrow\mathrm{Cu}\left(\mathrm{s} ight)$	+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
$\mathrm{Cr_2O_7}^{2-}\mathrm{(aq)} + 6\mathrm{e^-} + 14\mathrm{H^+}\mathrm{(aq)} \mathop{\longrightarrow} 2\mathrm{Cr^{3+}}\mathrm{(aq)} + 7\mathrm{H_2O}\mathrm{(l)}$	+1.33

Use the standard electrode potentials tabulated above to calculate the standard cell potentials due to the following reactions, giving your answers to 2 decimal places throughout:

### Part A (a)

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

### Part B (b)

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

### Part C (c)

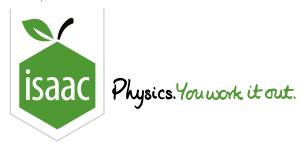
$$6\,\mathrm{Fe}^{2+}\,(\mathrm{aq}) + \mathrm{Cr}_2\mathrm{O_7}^{2-}\,(\mathrm{aq}) + 14\,\mathrm{H}^+\,(\mathrm{aq}) \longrightarrow 6\,\mathrm{Fe}^{3+}\,(\mathrm{aq}) + 2\,\mathrm{Cr}^{3+}\,(\mathrm{aq}) + 7\,\mathrm{H}_2\mathrm{O}\,(\mathrm{l})$$

### 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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Chemistry

Physical

Entropy

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# Essential Pre-Uni Chemistry H2.9



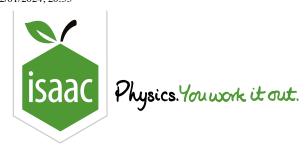
The displacement of hydrogen from acid by iron,

$$2\,\mathrm{H^{+}}\left(\mathrm{aq}
ight) + \mathrm{Fe}\left(\mathrm{s}
ight) \Longrightarrow \mathrm{Fe}^{2+}\left(\mathrm{aq}
ight) + \mathrm{H}_{2}\left(\mathrm{g}
ight)$$

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

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Chemistry

Physical

Electrochemistry

Essential Pre-Uni Chemistry L2.1

# Essential Pre-Uni Chemistry L2.1



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
$\mathrm{Fe^{2+}}\left(\mathrm{aq} ight)+2\mathrm{e^{-}}\longrightarrow\mathrm{Fe}\left(\mathrm{s} ight)$	-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
$\mathrm{Cr_2O_7}^{2-}\mathrm{(aq)} + 6\mathrm{e^-} + 14\mathrm{H^+}\mathrm{(aq)} \longrightarrow 2\mathrm{Cr}^{3+}\mathrm{(aq)} + 7\mathrm{H_2O}\mathrm{(l)}$	+1.33

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

#### Part A (a)

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

#### Part B (b)

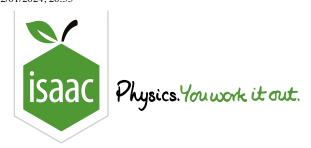
$$\mathrm{Zn}^{2+}\left(\mathrm{aq}\right)+2\,\mathrm{e}^{-}\longrightarrow\mathrm{Zn}\left(\mathrm{s}\right)$$

Part C (c)

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

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Gameboard

Chemistry

Physical Electrochemistry

Essential Pre-Uni Chemistry L2.2

# Essential Pre-Uni Chemistry L2.2



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
$\mathrm{Fe}^{2+}\left(\mathrm{aq} ight)+2\mathrm{e}^{-}\longrightarrow\mathrm{Fe}\left(\mathrm{s} ight)$	-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
$\mathrm{Cr_2O_7}^{2-}\mathrm{(aq)} + 6\mathrm{e^-} + 14\mathrm{H^+}\mathrm{(aq)} \mathop{\longrightarrow} 2\mathrm{Cr^{3+}}\mathrm{(aq)} + 7\mathrm{H_2O}\mathrm{(l)}$	+1.33

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

#### Part A (a)

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

#### Part B (b)

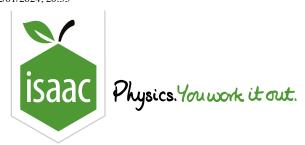
 $3\,Zn\left(s\right)+Cr_2O_7^{\,2-}\left(aq\right)+14\,H^+\left(aq\right)\longrightarrow 3\,Zn^{2+}\left(aq\right)+2\,Cr^{3+}\left(aq\right)+7\,H_2O\left(l\right). \label{eq:schrodinger}$  significant figures.

## Part C (c)

 $2\,Cr\left(s\right)+3\,Cu^{2+}\left(aq\right)\longrightarrow2\,Cr^{3+}\left(aq\right)+3\,Cu\left(s\right).\text{ Give your answer to 3 significant figures.}$ 

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Chemistry

Electrochemistry

Essential Pre-Uni Chemistry L1.7

# Essential Pre-Uni Chemistry L1.7

Physical



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
$\mathrm{Fe^{2+}}\left(\mathrm{aq} ight)+2\mathrm{e^{-}}\longrightarrow\mathrm{Fe}\left(\mathrm{s} ight)$	-0.44
$\mathrm{Cu}^{2+}\left(\mathrm{aq} ight) + \mathrm{e}^{-} \longrightarrow \mathrm{Cu}^{+}\left(\mathrm{aq} ight)$	+0.16
$\mathrm{Cu}^{2+}\left(\mathrm{aq} ight)+2\mathrm{e}^{-}\longrightarrow\mathrm{Cu}\left(\mathrm{s} ight)$	+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
$\mathrm{Cr_2O_7}^{2-}\left(\mathrm{aq} ight) + 6\mathrm{e^-} + 14\mathrm{H^+}\left(\mathrm{aq} ight) \longrightarrow 2\mathrm{Cr}^{3+}\left(\mathrm{aq} ight) + 7\mathrm{H_2O}\left(\mathrm{l} ight)$	+1.33

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

### Part A (a)

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

### Part B (b)

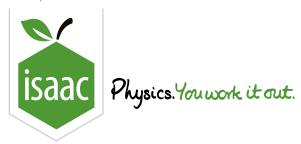
$$3 \operatorname{Fe}^{2+}(\operatorname{aq}) \longrightarrow 2 \operatorname{Fe}^{3+}(\operatorname{aq}) + \operatorname{Fe}(\operatorname{s})$$

## Part C (c)

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

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Gameboard

Chemistry

Physical

Electrochemistry

**Combining Potentials** 

## **Combining Potentials**



When half-cell potentials are combined to form a cell potential, the process is relatively straightforward: we balance the two half-equations to include the same number of electrons, and subtract the left-hand half-cell potential from the right-hand half-cell potential.

When two half-cell potentials need to be combined to instead form another half-cell potential, for a third half-reaction, the process is a little more complicated.

 $A^{(n_1+n_2)+} + n_1 e^- \longrightarrow A^{n_2+} \text{ has a half-cell potential of } x \text{ and } A^{n_2+} + n_2 e^- \longrightarrow A \text{ has a half-cell potential of } y.$ 

Derive an expression for the half-cell potential of the following reaction:

$$A^{(n_1+n_2)+}+(n_1+n_2)e^- {\:\longrightarrow\:} A$$

The following symbols may be useful: n\_1, n\_2, x, y

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