

# 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 by subtracting the reduction potential of the  side from the reduction potential of the  side. Standard reduction potentials can be tabulated, which correspond to values recorded under standard conditions against the standard  electrode. The 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:

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

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

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# Electrode Potential & Cell Potential 1

A Level



## Essential Pre-Uni Chemistry L1.1

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Name the element whose reduction is used as a standard by which all electrode potentials are measured.

- ☐ Hydrogen
- ☐ Iron
- ☐ Helium
- ☐ Lithium
- ☐ Platinum
- ☐ Oxygen
- ☐ Silver
- ☐ Fluorine

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# Electrode Potential & Cell Potential 3

**A Level**

## Essential Pre-Uni Chemistry L1.3

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The standard electrode potential,  $E^\ominus$ , for the reduction,  $\text{Br}_2(\text{aq}) + 2\text{e}^- \longrightarrow 2\text{Br}^-(\text{aq})$  is 1.09 V. Give the  $E^\ominus$  value for the reduction,  $\frac{1}{2}\text{Br}_2(\text{aq}) + \text{e}^- \longrightarrow \text{Br}^-(\text{aq})$ .

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# Electrode Potential & Cell Potential 4



## Essential Pre-Uni Chemistry L1.4

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

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# Electrode Potential & Cell Potential 5

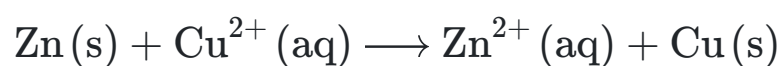


## Essential Pre-Uni Chemistry L1.5

Reduction	$E^\ominus / \text{V}$
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Zn}(\text{s})$	$-0.76$
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Cr}(\text{s})$	$-0.74$
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Fe}(\text{s})$	$-0.44$
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \longrightarrow \text{Cu}^+(\text{aq})$	$+0.16$
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$	$+0.34$
$\text{Cu}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Cu}(\text{s})$	$+0.52$
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	$+0.77$
$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$	$+0.80$
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{e}^- + 14\text{H}^+(\text{aq}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	$+1.33$

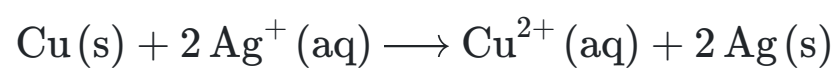
Use the standard electrode potentials tabulated above to calculate the standard cell potentials due to the following reactions, giving your answers to 2 decimal places throughout:

### Part A (a)



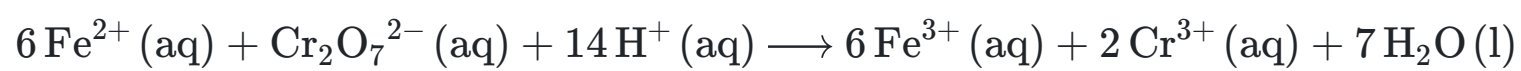
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**Part B (b)**



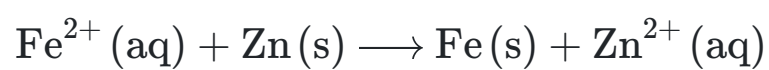
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**Part C (c)**



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**Part D (d)**



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# Free Energy Changes 9

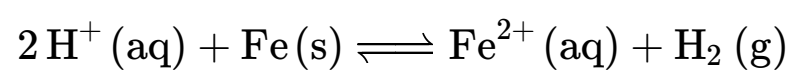
## Essential Pre-Uni Chemistry H2.9

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A Level



The displacement of hydrogen from acid by iron,



has a standard cell potential of 0.44 V. Find the associated standard Gibbs free energy change. (Faraday constant = 96 485 C mol<sup>-1</sup>)

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# Free Energy & Kc 1

## Essential Pre-Uni Chemistry L2.1

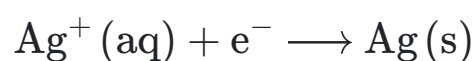
A Level



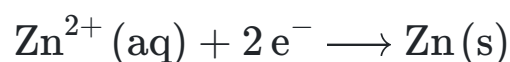
Reduction	$E^{\ominus} / \text{V}$
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \longrightarrow \text{Zn}(\text{s})$	$-0.76$
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^{-} \longrightarrow \text{Cr}(\text{s})$	$-0.74$
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^{-} \longrightarrow \text{Fe}(\text{s})$	$-0.44$
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \longrightarrow \text{Cu}(\text{s})$	$+0.34$
$\text{Cu}^{+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Cu}(\text{s})$	$+0.52$
$\text{Fe}^{3+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Fe}^{2+}(\text{aq})$	$+0.77$
$\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Ag}(\text{s})$	$+0.80$
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{e}^{-} + 14\text{H}^{+}(\text{aq}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	$+1.33$

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

### Part A (a)

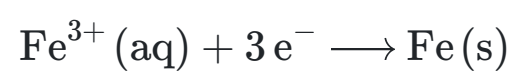


### Part B (b)



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**Part C** (c)



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# Free Energy & Kc 2

## Essential Pre-Uni Chemistry L2.2

A Level



Reduction	$E^{\ominus} / \text{V}$
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^{-} \longrightarrow \text{Zn}(\text{s})$	$-0.76$
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^{-} \longrightarrow \text{Cr}(\text{s})$	$-0.74$
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^{-} \longrightarrow \text{Fe}(\text{s})$	$-0.44$
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^{-} \longrightarrow \text{Cu}(\text{s})$	$+0.34$
$\text{Cu}^{+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Cu}(\text{s})$	$+0.52$
$\text{Fe}^{3+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Fe}^{2+}(\text{aq})$	$+0.77$
$\text{Ag}^{+}(\text{aq}) + \text{e}^{-} \longrightarrow \text{Ag}(\text{s})$	$+0.80$
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{e}^{-} + 14\text{H}^{+}(\text{aq}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	$+1.33$

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

### Part A (a)

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

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**Part B (b)**

$3 \text{Zn(s)} + \text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}^+(\text{aq}) \longrightarrow 3 \text{Zn}^{2+}(\text{aq}) + 2 \text{Cr}^{3+}(\text{aq}) + 7 \text{H}_2\text{O(l)}$ . Give your answer to 3 significant figures.

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**Part C (c)**

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

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# Electrode Potential & Cell Potential 7



## Essential Pre-Uni Chemistry L1.7

Reduction	$E^\ominus / \text{V}$
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Zn}(\text{s})$	$-0.76$
$\text{Cr}^{3+}(\text{aq}) + 3\text{e}^- \longrightarrow \text{Cr}(\text{s})$	$-0.74$
$\text{Fe}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Fe}(\text{s})$	$-0.44$
$\text{Cu}^{2+}(\text{aq}) + \text{e}^- \longrightarrow \text{Cu}^+(\text{aq})$	$+0.16$
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \longrightarrow \text{Cu}(\text{s})$	$+0.34$
$\text{Cu}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Cu}(\text{s})$	$+0.52$
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \longrightarrow \text{Fe}^{2+}(\text{aq})$	$+0.77$
$\text{Ag}^+(\text{aq}) + \text{e}^- \longrightarrow \text{Ag}(\text{s})$	$+0.80$
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 6\text{e}^- + 14\text{H}^+(\text{aq}) \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$	$+1.33$

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

**Part A** (a)



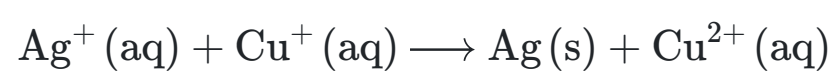
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**Part B (b)**



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**Part C (c)**



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# Combining Potentials

A Level

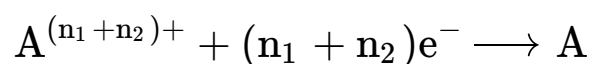


When half-cell potentials are combined to form a cell potential, the process is relatively straightforward: we balance the two half-equations to include the same number of electrons, and subtract the left-hand half-cell potential from the right-hand half-cell potential.

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.

$A^{(n_1+n_2)+} + n_1e^- \longrightarrow A^{n_2+}$  has a half-cell potential of  $x$  and  $A^{n_2+} + n_2e^- \longrightarrow A$  has a half-cell potential of  $y$ .

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



The following symbols may be useful:  $n_1$ ,  $n_2$ ,  $x$ ,  $y$