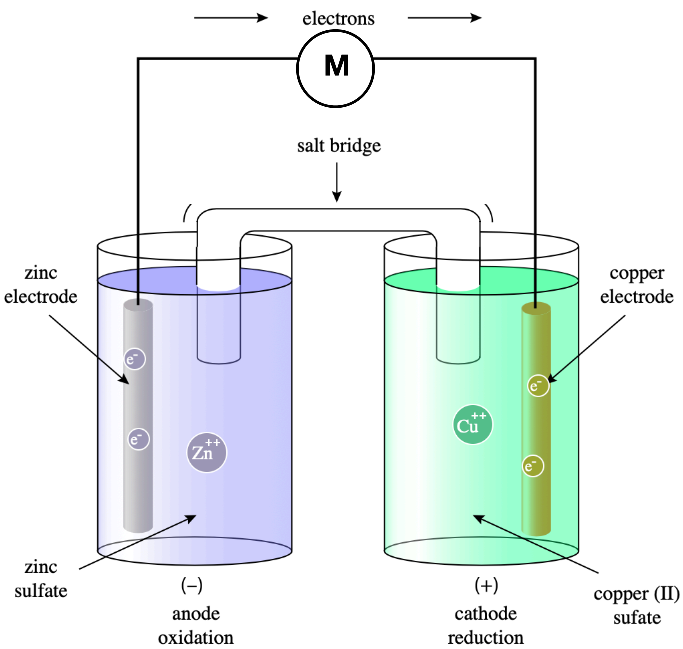
Understanding the relationship between $E^{\ominus}_{cell}$ and Gibbs energy change

The spontaneity or feasibility of a reaction can be described by both a positive $E^{\ominus}_{cell}$ value or a negative value for the change in Gibbs energy, $\Delta_rG^{\ominus}$, is it is no surprise that the two are mathematically related …

$\Delta_rG^{\ominus}$ for a reaction not only tells us if that reaction is spontaneous, but its value is also equivalent to the maximum amount of work a system can do. This makes is really useful for determining the electrical work that can be obtained from a chemical reaction in a battery or fuel cell.

Imagine an electrochemical cell where we replace the high resistance voltmeter with an electric motor, for example. The electrons flowing from the oxidation (negative) half cell to the reduction (positive) half cell can be used to do useful work.



The energy required to transfer charge around a circuit represents the electrical work that the electrochemical cell can perform.

charge (Q) = no. of mol of e- produced in the reaction (z) x Faraday constant (charge on 1 mol of e^- = 96500 $Cmol^{-1}$)

$Q = zF$

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It takes 1 joule of work to move 1 coulomb of charge through a potential difference of 1 volt.

electrical work (J) = - (charge x potential difference)

negative value because system loses energy as it does work

So if we combine these equations …

electrical work = $- zF E^{\ominus}_{cell}$

1J = 1C x 1V

comes from the change in Gibbs energy for the cell reaction, $\Delta_r G^{\ominus}$

charge

maximum potential difference between the two half cells that make up the electrochemical cell

$$\boxed{\Delta_r G^{\ominus} = - zF E^{\ominus}_{cell}}$$

Example:

Calculate $\Delta_r G^{\ominus}$ for the following reaction, under standard conditions, using standard electrode potential data

$$Fe^{2+}_{(aq)} + Ag^{+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Ag_{(s)}$$

$Ag^{+} + e^{-} \rightleftharpoons Ag$ $E^{\ominus} = +0.80V$ (reduction / positive half cell)

$Fe^{3+} + e^{-} \rightleftharpoons Fe^{2+}$ $E^{\ominus} = +0.77V$ (oxidation / negative half cell)

1 mol of e^{-} transferred

$E^{\ominus}_{cell} = +0.80 - 0.77 = +0.03V$

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$\Delta_r G^{\ominus}$ = - zF $E^{\ominus}_{cell}$

= - 1 x 96500 x (+0.03)

= - 2900 J mol^{-1}

= - 2.90 kJ mol^{-1}

the negative value means the reaction is feasible but as it is so small, even minor changes in the conditions of the reaction (temperature, concentration) will have a significant effect

Questions

Calculate $E^{\ominus}_{cell}$ for each of the following electrochemical cells, write an equation for the spontaneous reaction that occurs and calculate a value for $\Delta_r G^{\ominus}$.

(a) $Zn^{2+}_{(aq)}$ / $Zn_{(s)}$ and $Cd^{2+}_{(aq)}$ / $Cd_{(s)}$

(b) $Cu^{2+}_{(aq)}$ $Cu_{(s)}$ and $Cd^{2+}_{(aq)}$ / $Cd_{(s)}$

(c) $Ag^{+}_{(aq)}$ / $Ag_{(s)}$ and $Cd^{2+}_{(aq)}$ / $Cd_{(s)}$

Half cell	**$E^{\ominus}$ / V**
$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)}$	-0.76
$Cd^{2+}_{(aq)} + 2e^- \rightleftharpoons Cd_{(s)}$	-0.40
$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)}$	+0.34
$Ag^{+}_{(aq)} + e^- \rightleftharpoons Ag_{(s)}$	+0.80

Answers

(a) Zn^{2+}/Zn $E^\ominus = -0.76\,V$ oxid^n (−)

Cd^{2+}/Cd $E^\ominus = -0.40\,V$ red^n (+)

$E^\ominus_{cell} = -0.40 - (-0.76) = +0.36\,V$ ✓

$Zn_{(s)} + Cd^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cd_{(s)}$ ✓

$\Delta_r G^\ominus = -(2 \times 96500) \times (+0.36)$

$= -69000\ J\ mol^{-1}$

$= -69\ kJ\ mol^{-1}$ ✓

(b) Cu^{2+}/Cu $E^\ominus = +0.34\ V$ red^n

Cd^{2+}/Cd $E^\ominus = -0.40\ V$ oxid^n

$E^\ominus_{cell} = +0.34 - (-0.40) = +0.74\ V$ ✓

$Cd_{(s)} + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)} + Cd^{2+}_{(aq)}$ ✓

$\Delta_r G^\ominus = -(2 \times 96500) \times (+0.74)$

$= -143000\ J\ mol^{-1}$

$= -143\ kJ\ mol^{-1}$ ✓

(c) $Ag^+ / Ag \quad E^\ominus = +0.80\,V$ red^n

$Cd^{2+} / Cd \quad E^\ominus = -0.40\,V$ oxid^n

$$E^\ominus_{cell} = +0.80 - (-0.40)$$

$$= +1.20\,V$$

$$2Ag^+_{(aq)} + Cd_{(s)} \rightarrow Cd^{2+}_{(aq)} + 2Ag_{(s)}$$

$$\Delta_r G^\ominus = -(2 \times 96500) \times (+1.20)$$

$$= -232000\ J\,mol^{-1}$$

$$= -232\ kJ\,mol^{-1}$$