

Exercise walk-through

9.10

Cell Potential Under Nonstandard Conditions

AP Chemistry

Cell potential and electrolysis

Cell potential and free energy

$$E_{\text{cell}}^{\circ} = E_{\text{cath}}^{\circ} - E_{\text{an}}^{\circ}$$

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

Positive $E^{\circ} \Rightarrow$ negative ΔG (spontaneous). Zn-Cu:
 $0.34 - (-0.76) = +1.10 \text{ V}$.

Nernst & Faraday

$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

$$q = It, \quad n_{e^{-}} = \frac{q}{F}$$

A dead battery is $Q = K$, $E = 0$. **Electrolysis** : charge $\rightarrow$ mass of metal.

Coupling, the Nernst shift, and electrolysis

coupled reactions

an unfavourable reaction ($\Delta G > 0$) can be driven by a favourable one ($\Delta G < 0$) **sharing a common intermediate**

the condition

the total ΔG of the pair must be negative – ATP hydrolysis is the biological case

the Nernst equation

away from standard conditions the cell potential shifts with concentration

qualitatively

as reactants are consumed and products build up, the potential **falls** toward zero – a dead battery is a cell at equilibrium

electrolysis

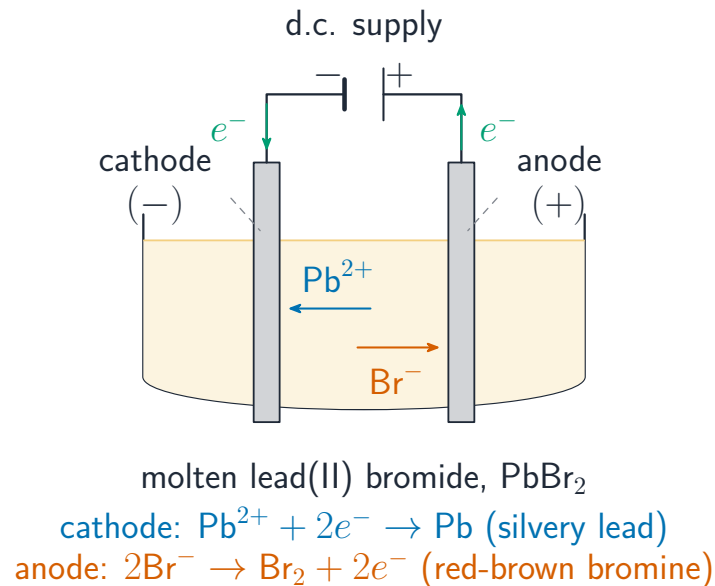
the **charge passed** determines how much substance is deposited – **Faraday's law**

the route

current $\times$ time $\rightarrow$ coulombs $\rightarrow$ moles of electrons $\rightarrow$ moles of substance $\rightarrow$ mass

A 2.0 A current for 30 minutes passes 3600 C, which is 0.0373 mol of electrons – and for Cu^{2+} that is **half** as many moles of copper.

Electrolysis



Electrolysis: ions move to the electrodes and are discharged

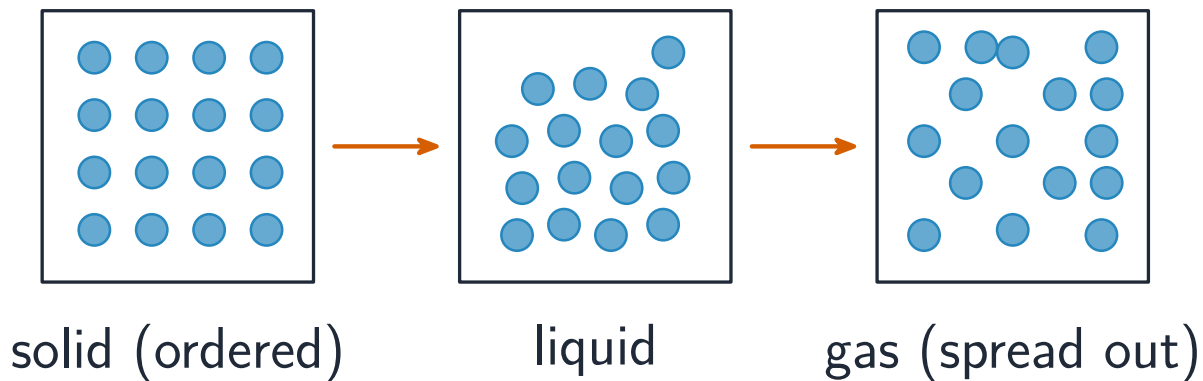
Galvanic and Electrolytic Cells, continued



Commercial batteries: galvanic cells convert chemical free energy into electrical work

Introduction to Entropy

entropy increases: $\Delta S > 0$



Entropy rises from solid to liquid to gas

Exercises 2.1-2.3

2.1 As a battery runs, does E rise or fall?

[1]

2.2 What is E when the cell reaches equilibrium?

[1]

2.3 Increasing a reactant's concentration does what to E ?

[1]

Exercises 2.1-2.3

2.1 As a battery runs, does E rise or fall? [1]

2.1

- Falls
-

2.2 What is E when the cell reaches equilibrium? [1]

2.2

- Zero
-

2.3 Increasing a reactant's concentration does what to E ? [1]

2.3

- Increases it

Exercise 3.1

3.1 When a galvanic cell reaches equilibrium, its cell potential is

[1]

☐

A at a maximum

B zero

C negative

D equal to E°

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3.1 When a galvanic cell reaches equilibrium, its cell potential is

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3.1 B

- zero

Exercise 3.2 (a)

3.2 For $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$:

(a) State the effect on E of increasing $[\text{Cu}^{2+}]$.

[2]

Exercise 3.2 (a)

3.2 For $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$:

(a) State the effect on E of increasing $[\text{Cu}^{2+}]$.

[2]

(a)

- Increasing $[\text{Cu}^{2+}]$ (a reactant) lowers Q , so E increases

Exercise 3.2 (b)

3.2 For $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$:

(b) State the effect on E of increasing $[\text{Zn}^{2+}]$.

[1]

Exercise 3.2 (b)

3.2 For $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$:

(b) State the effect on E of increasing $[\text{Zn}^{2+}]$.

[1]

(b)

- Increasing $[\text{Zn}^{2+}]$ (a product) raises Q , so E decreases

Exercise 3.3

3.3 Explain why the voltage of a battery gradually drops to zero as it is used. [2]

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3.3

- As the cell runs, reactants are used up and products accumulate, so Q rises toward K and E falls; at equilibrium $Q = K$ and $E = 0$