B9 · Electrolysis of aqueous solutions

Student notes - complete the underlined spaces | Notes 1/3

Decide what reacts at each electrode when water is present, explain the chloride exception and why E° must be used with caution, and predict products and observations.

Name: _____ Date: _____

1. Water joins the competition

Choose by table value

In B8 the cells held a molten salt, so only its ions could react. In a water solution, water is in the beaker too, and it can react at either electrode.

Water can be reduced: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$, _____. Water can be oxidized: $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$, which is the O_2 row run backward, from the _____ row.

At the cathode, the strongest oxidizing agent is reduced, and it has the _____ value. At the anode, the strongest reducing agent is oxidized, and it has the _____ value.

Na^+ (−2.71 V) is lower than water, so _____ is reduced at the cathode. It makes H_2 gas and _____, so the solution turns basic and the pH _____. Red litmus turns blue there. Sodium metal never forms from a water solution.

On the diploma: list every ion, and water. At the cathode pick the highest value. At the anode pick the lowest. Picking the highest at the anode is a common wrong choice.

Watch: Electrolysis of water (Tyler DeWitt, “Electrolysis”, 19:02)

Cathode examples

Cu^{2+} (+0.34 V) is higher than water, so _____ is reduced to copper metal. The cathode _____ mass and the blue colour fades as Cu^{2+} is used up.

The dividing line is −0.83 V. A cation above it, like Ag^+ or Cu^{2+}, is reduced before _____. A cation below it, like Na^+, Mg^{2+} or Al^{3+}, loses to water.

Zn^{2+} (−0.76 V) is just above the line, so it is predicted to win by a small margin. This is a prediction from the table, so compare numbers every time.

On the diploma: the wrong options usually reduce a metal that sits below water.

Cathode choices: Cu^{2+} +0.34 V or water −0.83 V. Reduced: _____

Anode choices: sulfate (not oxidized) or water +1.23 V. Oxidized: _____

Products: cathode _____; anode _____

Near the anode the pH _____ because H^+ is made.

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2. Anodes and the chloride exception

Choose the anode reaction

Take NaI(aq) with inert electrodes, which means electrodes that do not react, like carbon or platinum. I^- (+0.54 V) is lower than water (+1.23 V), so _____ is oxidized: $2I^- \rightarrow$ _____ + $2e^-$.

We observe a brown colour near the anode and infer that _____ forms. The Na^+ ions are spectator ions, which means they do not react at either electrode.

In $CuSO_4(aq)$, sulfate appears in the booklet only as a product, in the $S_2O_8^{2-}$ row at +2.01 V. That is higher than water, so sulfate is not oxidized and _____ is: $2H_2O \rightarrow O_2$ + _____ + $4e^-$.

Oxygen bubbles form, and H^+ is made, so the pH _____ near the anode. Blue litmus turns red there.

A reactive electrode can react itself. A copper anode (+0.34 V) is lower than water, so copper is the stronger reducing agent: $Cu \rightarrow Cu^{2+} + 2e^-$. The anode _____ and loses mass.

On the diploma: sulfate and nitrate are not oxidized, so water reacts. Always check what the electrode is made of. A wrong option ignores a reactive anode.

The chloride anomaly

In NaCl(aq), Cl^- is +1.36 V and water is +1.23 V. Water has the lower value, so the table predicts oxygen. But chlorine gas is _____: $2Cl^- \rightarrow Cl_2 + 2e^-$.

This is the chloride _____. The reason is overvoltage, the extra voltage some reactions need to run at a useful rate. Oxidizing water needs a _____ overvoltage than oxidizing chloride, so chloride reacts.

So think of a table value as a minimum, not a promise. E° values must be used with _____. The table minimum is _____ enough on its own, because an extra overvoltage must be applied.

On the diploma: write the table prediction first, then check for exceptions. In a chloride solution the observed product is chlorine gas. An option saying the table minimum is enough is a wrong choice.

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3. Predict products and observations

Sodium bromide

Take NaBr(aq) with inert electrodes. At the cathode, water (−0.83 V) beats Na^+ (−2.71 V), so _____ is reduced: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$.

At the anode, Br^- (+1.07 V) is lower than water (+1.23 V), so _____ is oxidized: $2Br^- \rightarrow Br_2 + 2e^-$. This is not a chloride case, so there is no exception.

Both halves move two electrons, so no multiplier is needed. The cell reaction is $2Br^- + 2H_2O \rightarrow Br_2 + H_2 +$ _____. Atoms and charge check: Br 2, H 4, O 2, charge −2 on each side.

E°cell = −0.83 − 1.07 = _____. The pH rises near the _____, because OH^- is made there.

On the diploma: E°cell is in volts, and the sign matters.

Observations and inferences

What we can see is an _____: bubbles at the cathode and a brown-orange colour near the anode.

Hydrogen gas, bromine and a rising pH are _____ from the half-reactions. A pH _____, a dye that changes colour with pH, can test the pH.

On the diploma: keep observation and inference apart. You see colour and bubbles. From them you work out each product.

Watch: Twice as much hydrogen as oxygen (Tyler DeWitt, “Electrolysis”, 22:58)

Copper sulfate and sodium sulfate

$CuSO_4(aq)$ with inert electrodes: copper forms at the _____, $Cu^{2+} + 2e^- \rightarrow Cu$. O_2 forms at the anode and the pH _____.

The water half moves four electrons and each copper half only two, so multiply the copper half by 2. Then add: $2Cu^{2+} + 2H_2O \rightarrow 2Cu + O_2 +$ _____.

E°cell = 0.34 − 1.23 = −0.89 V, so the source must supply more than 0.89 V. The blue colour fades and the solution turns more acidic.

$Na_2SO_4(aq)$: neither ion reacts, so water reacts at both electrodes. The ions only carry charge through the solution.

Double the cathode half to match four electrons: $4H_2O + 4e^- \rightarrow 2H_2 + 4OH^-$. Adding gives $6H_2O \rightarrow 2H_2 + O_2 + 4OH^- + 4H^+$.

The $4OH^-$ and $4H^+$ make $4H_2O$, so the overall reaction is $2H_2O \rightarrow$ _____ + O_2, a 2 : 1 ratio of H_2 to O_2.

On the diploma: expect the 2 to 1 ratio of H_2 to O_2 in a numerical-response item. H^+ on the product side means the pH goes down.

B9 · Practice

Electrolysis of aqueous solutions | Questions 1-3 of 12

State symbols: (s) solid, (aq) dissolved in water, (l) liquid, (g) gas. Use the supplied reaction and conditions. B4 values name the Alberta Chemistry 30 Data Booklet table where used.

B9-P01 · Easy · Explain why there are more possible reactions in an aqueous solution than in a molten salt.

B9-P02 · Easy · Given $NaNO_3(aq)$ with inert electrodes (Na^+ −2.71 V; water −0.83 V). Decide what is reduced at the cathode, write the half-reaction and state the change in pH near the cathode.

B9-P03 · Easy · Given $CuSO_4(aq)$ with inert electrodes (Cu^{2+} +0.34 V; water −0.83 V). Decide what is reduced at the cathode and predict the change in mass of the cathode and the colour of the solution near it.

B9 · Practice

Electrolysis of aqueous solutions | Questions 4-6 of 12

B9-P04 · Easy · Given NaI(aq) with inert electrodes (I_2/I^- +0.54 V; O_2/H_2O +1.23 V). Decide what is oxidized at the anode, write the half-reaction and describe the observation and the inference.

B9-P05 · Medium · In $CuSO_4$(aq) with inert electrodes, water is oxidized at the anode. Write the half-reaction and predict the observation at the anode and the change in pH near it.

B9-P06 · Medium · Given $CuSO_4$(aq) with a copper anode and an inert cathode (Cu^{2+}/Cu +0.34 V; O_2/H_2O +1.23 V). Decide what is oxidized at the anode and predict the change in its mass.

B9 · Practice

Electrolysis of aqueous solutions | Questions 7-9 of 12

B9-P07 · Medium · Aqueous NaCl is electrolyzed with inert electrodes. State the product at the anode that the table predicts, the product that is observed, and the reason for the difference.

B9-P08 · Medium · Given NaBr(aq) with inert electrodes (water −0.83 V; Br_2/Br^- +1.07 V; O_2/H_2O +1.23 V). Write the cell reaction and calculate E°cell.

B9-P09 · Challenging · Given $CuSO_4(aq)$ with inert electrodes. Match the electrons in the half-reactions, write the cell reaction and calculate E°cell (Cu^{2+}/Cu +0.34 V; O_2/H_2O +1.23 V).

B9 · Practice

Electrolysis of aqueous solutions | Questions 10-12 of 12

B9-P10 · Challenging · Given $Na_2SO_4(aq)$ with inert electrodes. Write the half-reactions with matched electrons and the overall reaction, and say which gas forms in the larger amount.

B9-P11 · Challenging · A student says that applying the minimum voltage from the table guarantees the predicted reaction. Use aqueous NaCl to explain why this is not correct.

B9-P12 · Challenging · Given $AgNO_3(aq)$ with inert electrodes (Ag^+ +0.80 V; water −0.83 V; O_2/H_2O +1.23 V). State what is reduced and what is oxidized and write the cell reaction.