Chemguide – answers

MAKING PREDICTIONS USING REDOX POTENTIALS

1. In each diagram below, the substances circled are what you are starting with, and the arrows show the directions the equilibria would move as electrons are transferred according to the E^0 values. The more negative (or less positive) equilibrium will move to the left. The more positive (or less negative) one will move to the right.

a) The reaction is feasible.

$$Pb^{2+}_{(aq)} + 2e^- \rightleftharpoons Pb_{(s)} \qquad E^0 = -0.13\ v$$

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \qquad E^0 = -0.76\ v$$

Since you are starting with zinc and lead(II) ions, movements as shown will produce a reaction.

b) The reaction is feasible.

$$Cu^{2+}_{(aq)} + 2e^- \rightleftharpoons Cu_{(s)} \qquad E^0 = +0.34\ v$$

$$Ag^{+}_{(aq)} + e^- \rightleftharpoons Ag_{(s)} \qquad E^0 = +0.80\ v$$

The copper and silver equilibria can move in the direction they want, and so the reaction will be feasible.

c) The reaction is not feasible.

$$V^{3+}_{(aq)} + e^- \rightleftharpoons V^{2+}_{(aq)} \qquad E^0 = -0.26\ v$$

$$Sn^{2+}_{(aq)} + 2e^- \rightleftharpoons Sn_{(s)} \qquad E^0 = -0.14\ v$$

The vanadium equilibrium has the greater tendency to move to the left, but if you start with vanadium(III) ions, that is where it is already. To get any reaction, the equilibria would have to move in the wrong directions.

d) The reaction is feasible.

$$V^{3+}_{(aq)} + e^- \rightleftharpoons V^{2+}_{(aq)} \qquad E^0 = -0.26\ v$$

$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \qquad E^0 = -0.76\ v$$

Movement is possible in the directions wanted by the E^0 values.

e) The reaction is feasible.

$$Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6e^- \rightleftharpoons 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)} \quad E^0 = +1.33\text{ v}$$

$$Fe^{3+}{}_{(aq)} + e^- \rightleftharpoons Fe^{2+}{}_{(aq)} \quad E^0 = +0.77\text{ v}$$

The dichromate(VI) equilibrium has the greater tendency to move to the right, forcing the iron one to the left. Both of those movements are possible.

f) The reaction is feasible.

$$Fe^{3+}{}_{(aq)} + e^- \rightleftharpoons Fe^{2+}{}_{(aq)} \quad E^0 = +0.77\text{ v}$$

$$O_{2(g)} + 4H^+{}_{(aq)} + 4e^- \rightleftharpoons 2H_2O_{(l)} \quad E^0 = +1.23\text{ v}$$

The same argument applies as in the previous example.

g) The reaction isn't feasible.

$$PbO_{2(s)} + 4H^+{}_{(aq)} + 2e^- \rightleftharpoons Pb^{2+}{}_{(aq)} + 2H_2O_{(l)} \quad E^0 = +1.47\text{ v}$$

$$O_{2(g)} + 4H^+{}_{(aq)} + 4e^- \rightleftharpoons 2H_2O_{(l)} \quad E^0 = +1.23\text{ v}$$

The more positive E^0 for the lead equilibrium means that it will have the greater tendency to move to the right. But that is where it is already. No reaction is possible without moving the equilibria in the opposite way to that required by the E^0 values.

h) The reaction is feasible.

$$PbO_{2(s)} + H_2O_{(l)} + 2e^- \rightleftharpoons PbO_{(s)} + 2OH^-{}_{(aq)} \quad E^0 = +0.28\text{ v}$$

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \rightleftharpoons 4OH^-{}_{(aq)} \quad E^0 = +0.40\text{ v}$$

The oxygen equilibrium has the more positive E^0 value and moves to the right. The lead equilibrium is less positive and moves to the left. Both of these are possible moves, given what you start with.

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2. If you are going to oxidise VO^{2+} to VO_2^+, you need to make this equilibrium go to the left. That means that you would have to couple it with an equilibrium which has a more positive E^0 value - one which is greater than +1.00 v. That equilibrium would then move to the right, and the one we are interested in would move to the left.

   From Q1, the possibilities are

$$Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6e^- \rightleftharpoons 2Cr^{3+}{}_{(aq)} + 7H_2O_{(l)} \qquad E^0 = +1.33\ v$$

$$O_{2(g)} + 4H^+{}_{(aq)} + 4e^- \rightleftharpoons 2H_2O_{(l)} \qquad E^0 = +1.23\ v$$

$$PbO_{2(s)} + 4H^+{}_{(aq)} + 2e^- \rightleftharpoons Pb^{2+}{}_{(aq)} + 2H_2O_{(l)} \qquad E^0 = +1.47\ v$$

   That means that you could use:

   - an acidified solution containing dichromate(VI) ions; (To be strictly accurate, you would use potassium dichromate(VI) solution acidified with dilute sulphuric acid, but for the purposes of this question, I would be happy if you just quoted the necessary ions.)
   - oxygen bubbled through an acidified solution of the VO^{2+} ions; (You mustn't forget to include the hydrogen ions from the left-hand side of the oxygen equilibrium. They have got to be there.)
   - lead(IV) oxide added to an acidified solution of the VO^{2+} ions. (Again, don't forget the hydrogen ions.)

3.

$$MnO_{2(s)} + 4H^+{}_{(aq)} + 2e^- \rightleftharpoons Mn^{2+}{}_{(aq)} + 2H_2O_{(l)} \qquad E^0 = +1.23\ v$$

$$Cl_{2(g)} + 2e^- \rightleftharpoons 2Cl^-{}_{(aq)} \qquad E^0 = +1.36\ v$$

   These are standard redox potentials, implying that all ion concentrations are 1 mol dm^{-3}.

   With dilute hydrochloric acid, the MnO_2 E^0 value isn't positive enough for that equilibrium to move to the right, and the chlorine one to the left - so there is no reaction.

   At higher concentrations, the positions of the two equilibria will change according to Le Chatelier's Principle. The extra concentration of hydrogen ions will push the MnO_2 equilibrium further to the right, increasing the E value. At the same time, the extra chloride ions will push that equilibrium further to the left, decreasing that E value.

   Under these circumstances, the more positive value becomes the MnO_2 one, and so the reaction becomes feasible, with that equilibrium moving to the right, and the chlorine one to the left, producing chlorine gas.

4. The reaction may not happen if there is a very high activation energy.