Galvanic cells:

13-7. Explain how a galvanic cell uses a spontaneous chemical reaction to generate electricity.

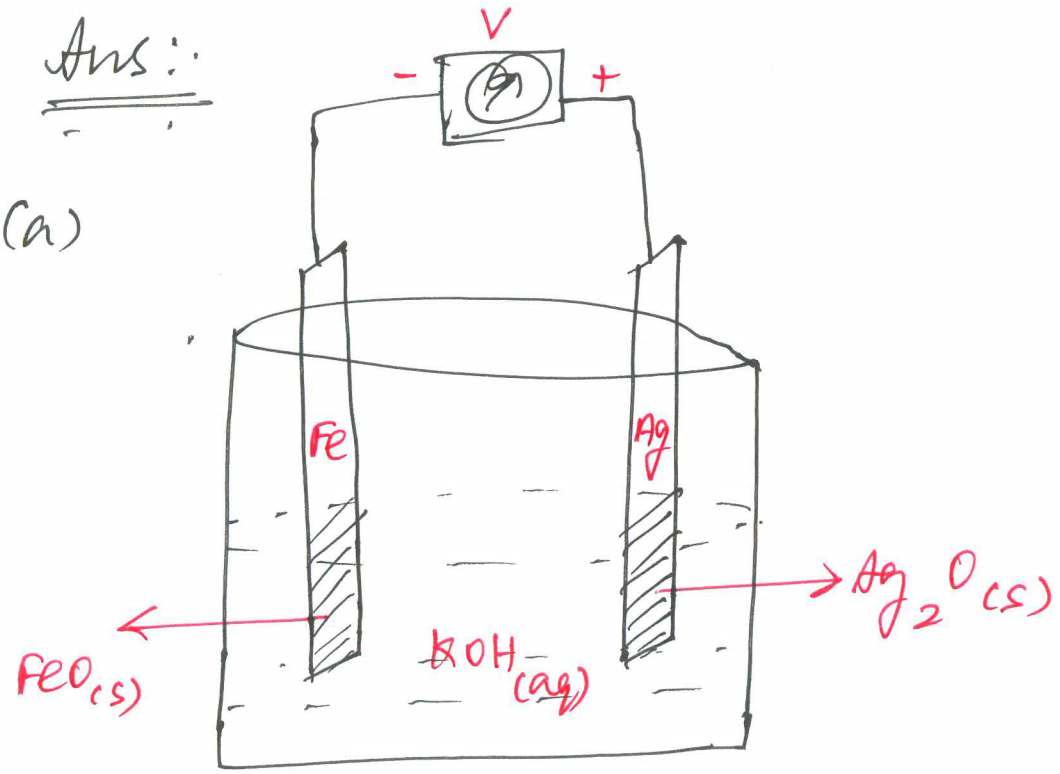
Ans:

In a galvanic cell two half-reactions are physically separated from each other. At the anode, an oxidation reaction generates electrons that can flow through the electric circuit to reach the cathode, where a reduction reaction occurs. The favorable free energy change for the net reaction provides the driving force for electrons to flow through the circuit. There must be a connector (such as a salt bridge) between the two half-cells to allow ions to flow to maintain electroneutrality.

13-8 For each cell pictured, write a line notation to describe it. Write an oxidation reaction for the left electrode and a reduction reaction for the right electrode.

Ans:

(a)

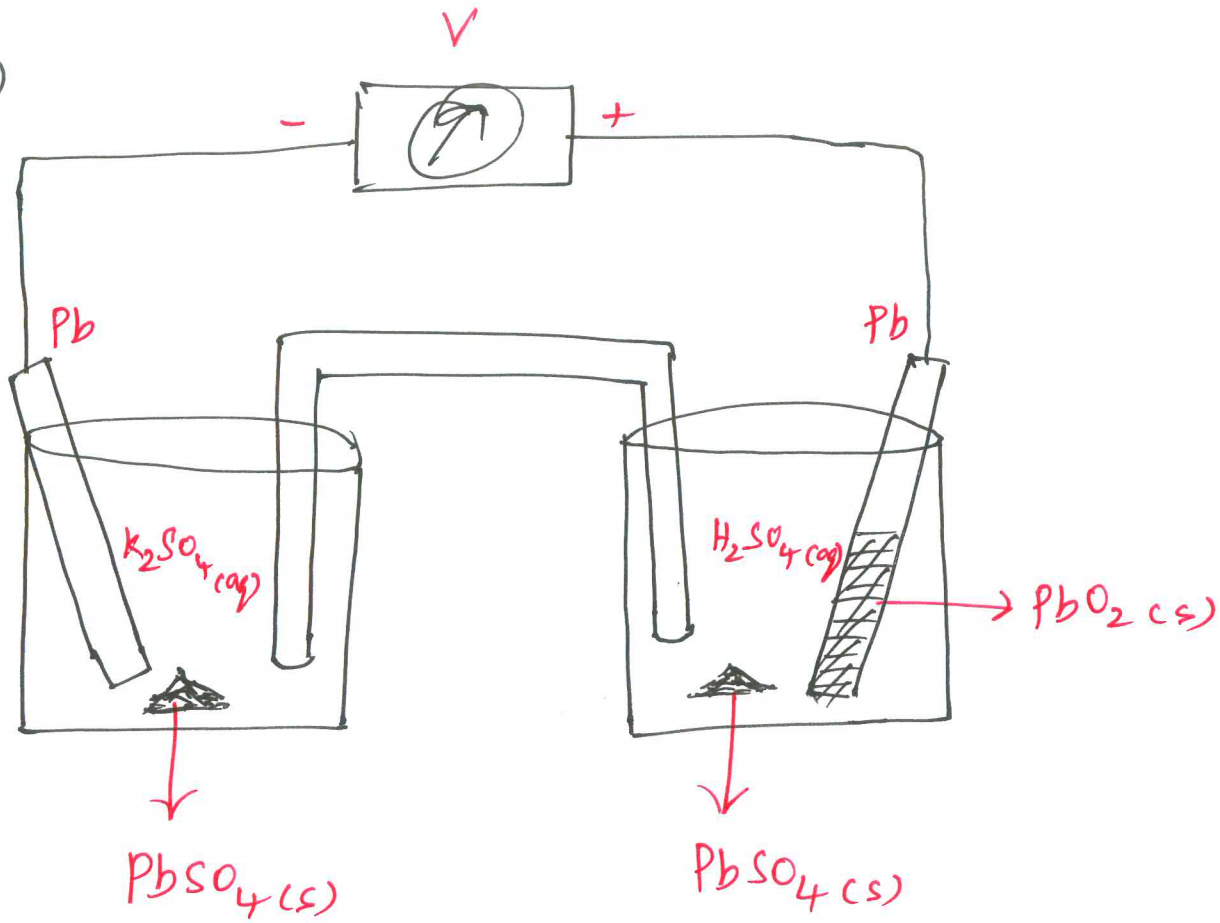


(a) $Fe_{(s)} \mid FeO_{(s)} \mid KOH_{(aq)} \mid Ag_2O_{(s)} \mid Ag_{(s)}$

Oxidation: $Fe_{(s)} + 2OH^- \rightleftharpoons FeO_{(s)} + H_2O + 2e^-$

Reduction: $Ag_2O + H_2O + 2e^- \rightleftharpoons 2Ag_{(s)} + 2OH^-$

(b)



Ans:

$$Pb_{(s)} \mid PbSO_{4(s)} \mid K_2SO_{4(aq)} \,\|\, H_2SO_{4(aq)} \mid PbSO_{4(s)} \mid PbO_{2(s)} \mid Pb_{(s)}$$

Oxidation:

$$Pb_{(s)} + SO_4^{2-} \rightleftharpoons PbSO_{4(s)} + 2e^-$$

Reduction:

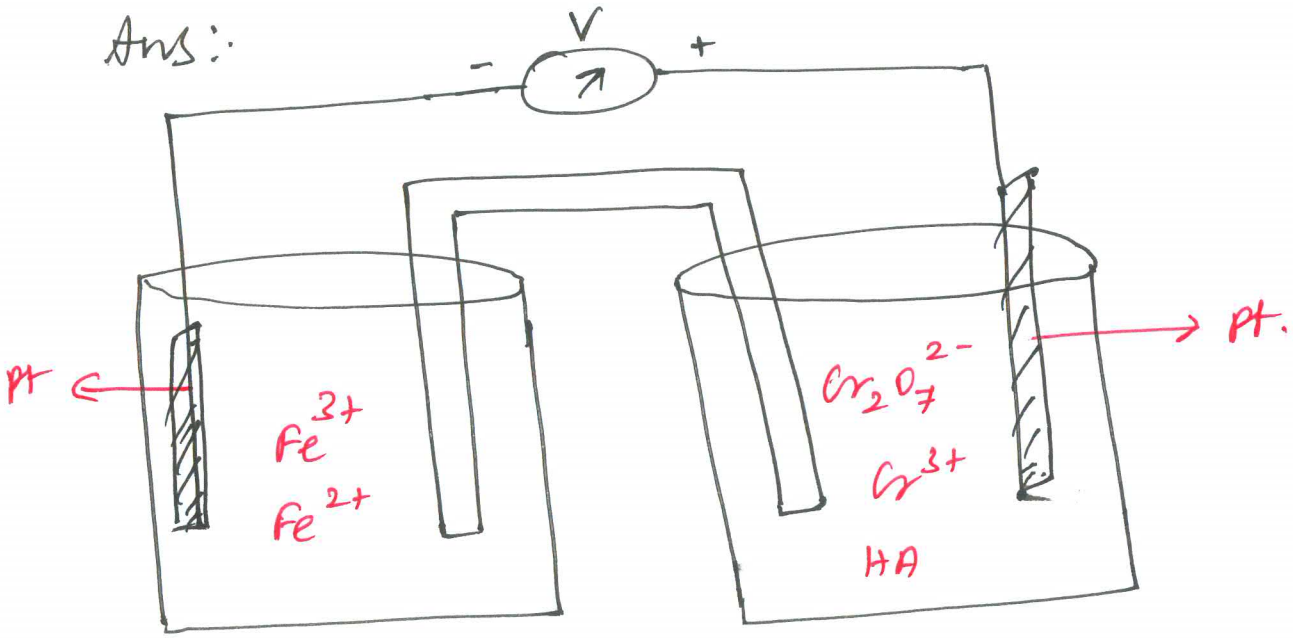
$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightleftharpoons PbSO_{4(s)} + 2H_2O$$

13-9:

(a) Draw a picture of the following cell, showing the location of each species:

$$Pt_{(s)} \mid Fe^{3+}_{(aq)}, Fe^{2+}_{(aq)} \parallel Cr_2O_7^{2-}{}_{(aq)}, Cr^{3+}_{(aq)}, HA_{(aq)} \mid Pt_{(s)}$$

Ans:



(b) write an oxidation for the left half-cell and a reduction for the right half-cell.

Ans:

oxidation: $Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$

Reduction: $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O$

(c) write a balanced equation for the net cell reaction.

Ans:

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \rightleftharpoons 2Cr^{3+} + 6Fe^{3+} + 7H_2O.$$

13-10: A light weight rechargeable battery uses the following cell:

$$Zn_{(s)} \mid ZnCl_{2\,(aq)} \parallel Cl^-_{(aq)} \mid Cl_{2(l)} \mid C_{(s)}$$

(a) write an oxidation for the left half-cell and a reduction for the right half cell.

Ans:

Oxidation : $Zn_{(s)} \rightleftharpoons Zn^{2+} + 2e^-$

Reduction : $Cl_{2\,(l)} + 2e^- \rightleftharpoons 2Cl^-$

(1b)

(b) If the battery delivers a constant current of 1.00×10^3 A for 1.00 h, how many kilograms of Cl_2 will be consumed?

Ans:

One mol of Cl_2 requires 2 mol of e^-.

Moles of Cl_2 consumed in 1.00 hr

$$= \frac{1}{2} (\text{mol of } e^-/\text{hr})$$

$$= \left[\frac{1}{2} \left(1.00 \times 10^3 \frac{C}{s}\right) \Big/ \left(9.64 \times 10^4 \frac{C}{\text{mol}}\right) \right] (3600\ s/\text{hr})$$

$$= 18.7 \text{ mol of } Cl_2$$

$$= 1.32 \text{ kg}.$$

Standard Potentials:

13-12. Which will be the strongest oxidising agent under standard conditions (ie all activities = 1)

HNO_2, Se, UO_2^{2+}, Cl_2, H_2SO_4 or MnO_2?

Ans:

Cl_2 is strongest because it has the most +ve reduction potential.

Example: Use Le Chatelier's principle and half reactions from Appendix H to find which of the following become stronger oxidising agents as the pH is lowered. Which are unchanged, and which become weaker?

Cl_2
Chlorine

$Cr_2O_7^{2-}$
Dichromatate

Fe^{3+}
Ferric

MnO_4^-
Permanganate

IO_3^-
Jodate.

Ans:

Become stronger : $Cr_2O_7^{2-}$, MnO_4^-, IO_3^-

Unchanged : Cl_2, Fe^{3+}.

13-13:

(a) In the presence of cyanide ion, the reduction potential of Fe(III) is decreased from 0.771 to 0.356 V.

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+} \qquad E^0 = 0.771\ V.$$

Ferric — Ferrous

$$Fe(CN)_6^{3-} + e^- \rightleftharpoons Fe(CN)_6^{4-} \qquad E^0 = 0.356\ V$$

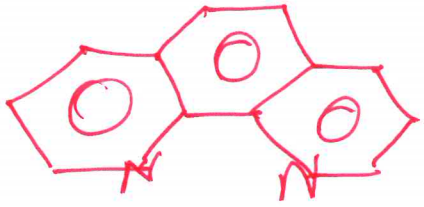
Ferricyanide — Ferrocyanide

Which ion, Fe^{3+} or Fe^{2+}, is stabilized more by complexing with CN^-?

Ans:

Since it is harder to reduce Fe(III) to Fe(II) in the presence of CN^- Fe(III) is stabilized more than Fe(II).

(b) using Appendix H, answer the same question when the ligand is phenanthroline instead of cyanide.



Phenanthroline.

Ans:

Since it is easier to reduce Fe(III) to Fe(II) in the presence of phenanthroline, Fe(II) is stabilized more than Fe(II).