

13-6

## ~~13-6~~. Cells as Chemical probes:

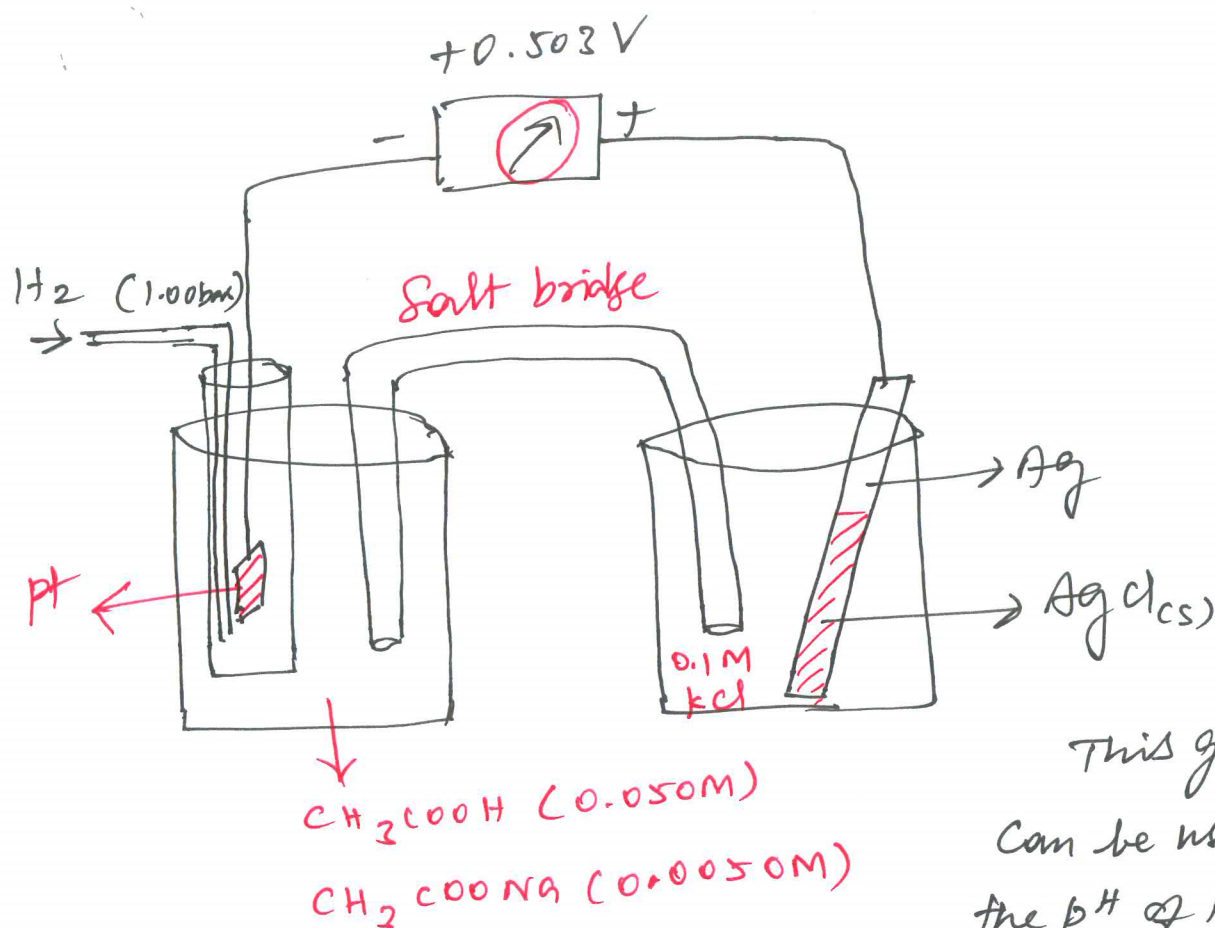
(1)

It is essential to distinguish two classes of equilibria associated with Galvanic cells:

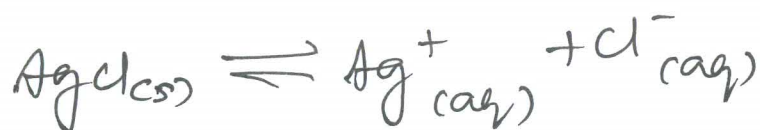
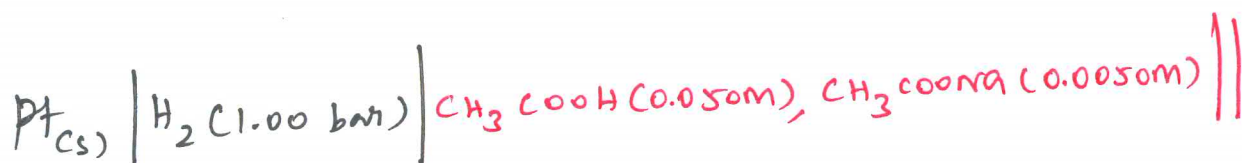
1. Equilibrium between the two half cells.
2. Equilibrium within each half cell.

If a galvanic cell has a nonzero voltage, then the net cell reaction is not at equilibrium. We say that equilibrium between the two half-cells has not been established.

However, we do allow the half-cells to stand long enough to come to chemical equilibrium within each half-cell.



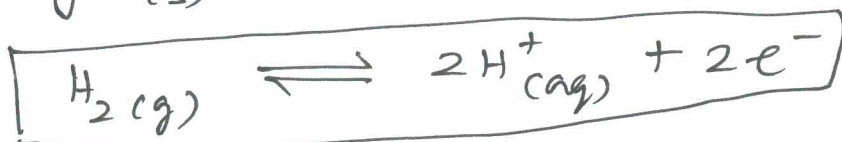
This galvanic cell can be used to measure the pH of the left half-cell



Right:

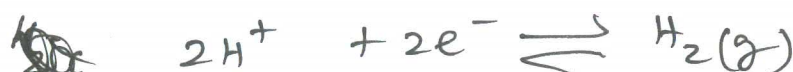


$$E^{\circ}_{+} = 0.222\text{V}$$



$$E^{\circ}_{-} = 0\text{V}$$

Left:



(3)

The net cell reaction is not at equilibrium, because the measured voltage is 0.503V, not 0V.

∴ The Nernst equation for the cell reaction is

$$E = E_+ - E_-$$

$$= \left( 0.222 - \frac{0.05916}{2} \log [Cu^+]^2 \right) -$$

$$\left( 0 - \frac{0.05916}{2} \log \frac{1.00}{[H^+]^2} \right)$$

$$\therefore 0.503 = \left( 0.222 - 0.05916 \log [Cu^+] \right) -$$

$$\left( 0 - \frac{0.05916}{2} \log \frac{1.00}{[H^+]^2} \right)$$

$$0.503 = \left( 0.222 - 0.05916 \log (0.10) \right) -$$

$$\left( 0 - \frac{0.05916}{2} \log \frac{1.00}{[H^+]^2} \right)$$

$$\therefore E = 0.503V$$

$$\log x^n = n \log x$$

$$\therefore [Cu^+] = 0.101$$

(4)

$$\therefore 0.503 = 0.222 - 0.05916(-1) + 0.02958(0 - 2\log[H^+])$$

$$0.503 = 0.2812 - 0.05916 \log[H^+]$$

$$0.2218 = -0.05916 \log[H^+]$$

$$\therefore -\log[H^+] = \frac{0.2218}{0.05916} = 3.749$$

$$\therefore \log[H^+] = -3.75$$

$$\therefore [H^+] = 10^{-3.75}$$

$$[H^+] = 1.8 \times 10^{-4} \text{ M}$$

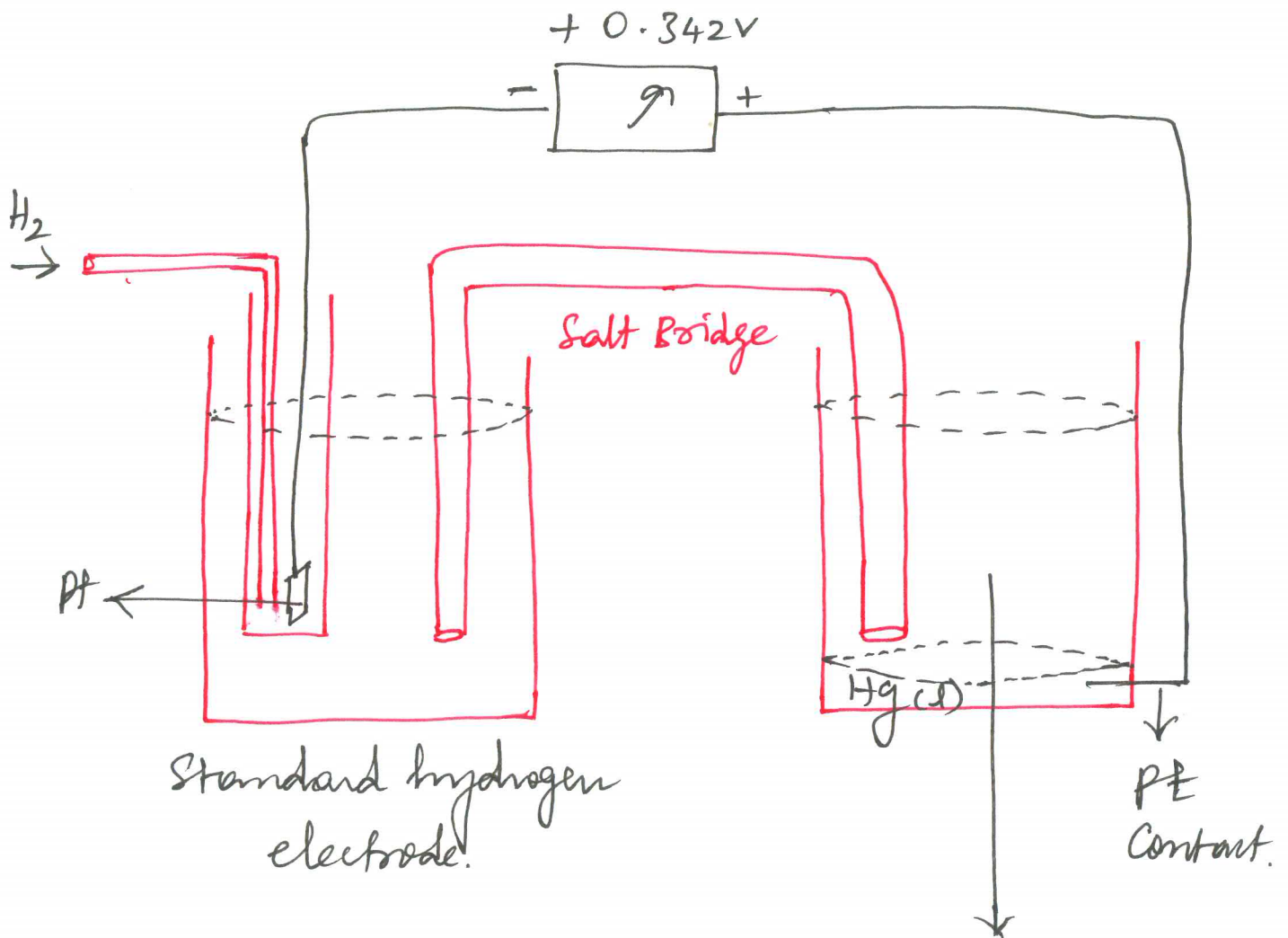
now we can calculate the equilibrium constant for the acid-base reaction that has come to equilibrium in the left half-cell.

$$\therefore K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = \frac{(0.0050)(1.8 \times 10^{-4})}{0.050}$$

$$\therefore \boxed{K_a = 1.8 \times 10^{-5}}$$

(5)

A galvanic cell that can be measure the formation constant for  $\text{Hg}(\text{EDTA})$ :

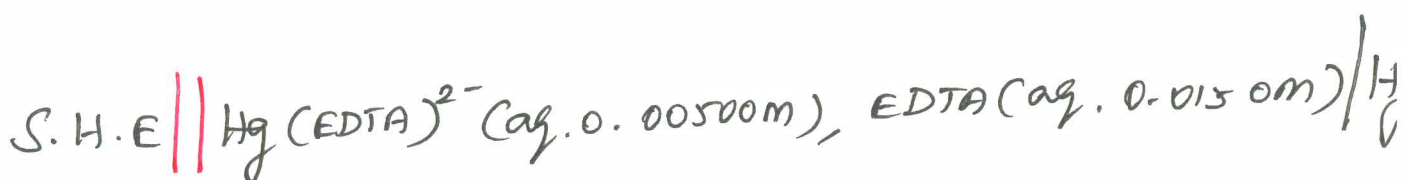


Solution prepared from

50.0 mL of 0.0100 M  $\text{HgCl}_2$

40.0 mL of 0.050 M EDTA

10.0 mL of buffer  $\text{pH}$  6.00



This values from the problems.



(b)

Example :-

The above cell measures the formation constant  $K_f$  of  $\text{Hg}(\text{EDTA})^{2-}$ . The solution in the right hand compartment contains 0.500 mmol of  $\text{Hg}^{2+}$  and 2.00 mmol of EDTA in a volume of 0.100 L buffered to pH 6.00. The voltage is +0.342 V. Find the value of  $K_f$  for  $\text{Hg}(\text{EDTA})^{2-}$ .

Solution :-

Step 1:

The left half-cell is a S.H.E for which

$$E_- = 0.$$

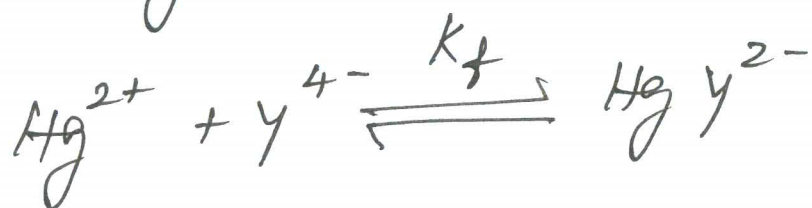
In the right half-cell, mercury is in two oxidation states. So let's write the half reaction.



(7)

$$E_+ = 0.852 - \frac{0.05916}{2} \log \frac{1}{[Hg^{2+}]}$$

In the right half cell, the reaction between  $Hg^{2+}$  and EDTA is



Because we expect  $K_f$  to be large, we assume that all the  $Hg^{2+}$  has reacted to make  $HgY^{2-}$ .

$$\therefore \text{The Concentration of } HgY^{2-} = \frac{0.500 \text{ mmol}}{100 \text{ mL}} = 0.00500 \text{ M}.$$

The remaining EDTA has a total concentration of

$$\frac{(2.00 - 0.50) \text{ mmol}}{100 \text{ mL}} = \frac{1.5 \text{ mmol}}{100 \text{ mL}} = 0.015 \text{ M}$$

(8)

∴ The right hand component therefore contains

0.00500 M of  $\text{HgY}^{2-}$

0.015 M of EDTA

and a small, unknown amount of  $\text{Hg}^{2+}$ .



∴ The formation constant for  $\text{HgY}^{2-}$  can be written

$$K_f = \frac{[\text{HgY}^{2-}]}{[\text{Hg}^{2+}][\text{Y}^{4-}]}$$

$$= \frac{[\text{HgY}^{2-}]}{[\text{Hg}^{2+}] \alpha_{\text{Y}^{4-}} [\text{EDTA}]}$$

now we know the concentration of  $[\text{HgY}^{2-}]$ ,  $[\text{EDTA}]$ , all we need to find is  $[\text{Hg}^{2+}]$  in order to evaluate  $K_f$ .

$$\therefore [\text{Y}^{4-}] = \alpha_{\text{Y}^{4-}} [\text{EDTA}]$$

$$[\text{HgY}^{2-}] = 0.00500 \text{ M}$$

$$[\text{EDTA}] = 0.0150 \text{ M}$$

$$\alpha_{\text{Y}^{4-}} \text{ at } \text{pH} = 6$$

$$= 1.8 \times 10^{-5}$$



(9)

Step 2:

The Nernst equation for the net cell reaction is

$$E = E_+ - E_-$$

$$\therefore 0.342 = E_+ - E_-$$

$$0.342 = \left[ 0.852 - \frac{0.05916}{2} \log \frac{1}{[\text{Hg}^{2+}]} \right] - 0$$

$$\therefore \Rightarrow [\text{Hg}^{2+}] = 5.7 \times 10^{-18} \text{ M.}$$

Step 3:

now we have all the values. Therefore we can evaluate the formation constant for  $\text{HgY}^{2-}$ .

$$K_f = \frac{[\text{HgY}^{2-}]}{[\text{Hg}^{2+}] \alpha_{Y^{4-}} [\text{EDTA}]}$$

$$= \frac{(0.00500)}{(5.7 \times 10^{-18})(1.8 \times 10^{-5})(0.0150)}$$

$$= 3 \times 10^{21}$$

$$\therefore K_f = 3 \times 10^{21}$$

The mixture of EDTA + Hg(EDTA)<sup>2-</sup> in the cathode serves as a mercuric ion "buffer" that fixes the concentration of Hg<sup>2+</sup>. This concentration, in turn, determines the cell voltage.

(11)

The procedure for writing a reactions to find out the unknown concentration to solve the chemical equilibrium problem:

Step 1: write the two half-reaction and their standard potentials.

Step 2: write a Nernst equation for the net reaction and put in all the known quantities. If all is well, there will be only one unknown in the equation.

Step 3: Find out unknown concentration and use that concentration to solve the chemical equilibrium problem.