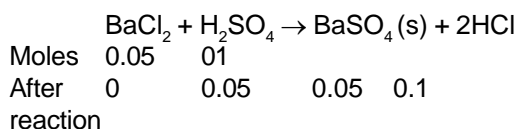


CHEMISTRY

1. $n_{\text{BaCl}_2} = \frac{20.8}{100} \times \frac{50}{208} = \frac{1}{20} = 0.05$; $n_{\text{H}_2\text{SO}_4} = \frac{9.8}{100} \times \frac{100}{98} = 0.1$



$$\Rightarrow n_{\text{SO}_4^{2-}} \text{ remaining} = 0.05 \quad \Rightarrow [\text{SO}_4^{2-}] = \frac{0.05}{150} \times 1000 = \frac{1}{3} = 0.33$$



$$n_{\text{Cl}_2} = \frac{1.12}{22.4} = \frac{1}{20} \quad \Rightarrow n_{\text{HCl}} = 4 \times \frac{1}{20} = \frac{1}{5}$$

$$\Rightarrow m_{\text{HCl}} = \frac{1}{5} \times 36.5 = V \times 1.2 \times \frac{3.65}{100} \quad \Rightarrow V = 166.7 \text{ ml}$$

3. In case of HCl, greater volume of KMnO_4 is used while in case of HNO_3 , lesser volume of KMnO_4 is used, than appropriate.

4. From law of equivalence,
 Eq of KMnO_4 (v.f. = 5) = Eq. of SO_2 (v.f. = 2)

$$\frac{1.58}{158} \times 5 \times 2 = n_{\text{SO}_2} \times 2$$

$$\therefore n_{\text{SO}_2} = 0.05 \text{ moles} \quad ; \quad \text{Whole of S from FeS}_2 \text{ is converted into SO}_2$$

\therefore Applying POAC on S:

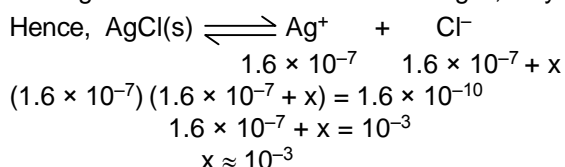
$$2 \times n_{\text{FeS}_2} = 1 \times n_{\text{SO}_2}$$

$$\therefore 2 \times \frac{m_{\text{FeS}_2}}{120} = 1 \times 0.05 \quad \therefore m_{\text{FeS}_2} = 3 \text{ g} = x \quad \therefore x = 3$$

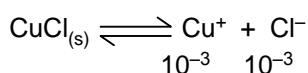
5. meq. of NH_2OH = meq. of $\text{K}_2\text{Cr}_2\text{O}_7$
 $\therefore V \times M \times 2 = V \times 6 \times 0.5 \quad \therefore M = 1.5$

6. If the unknown sample contains equimolar mixture of NaOH and Na_2CO_3 , then $V_P = 2V_M$.

7. It is logical to see that out of 0.1 mol AgCl , only 1.6×10^{-7} moles passed into the solution.

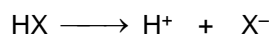


x is the concentration of Cl^- due to CuCl .



$$K_{\text{sp}} = 10^{-6}$$

8. $\text{pH} = 2 \Rightarrow [\text{H}^+] = 0.01 \text{ M}$

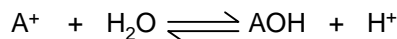


$$0.01$$

$$\text{finally } \approx 0 \quad 0.01 \quad 0.01$$

Hence, HX is strong acid.

$$[\text{A}^+] = 0.01$$



$$t = 0 \quad 0.01$$

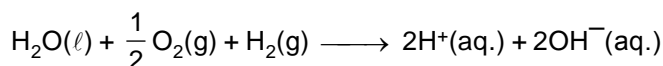
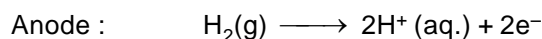
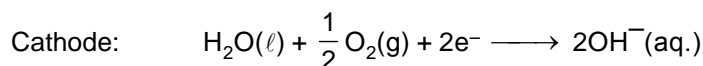
$$\text{final } \approx 0 \quad 0.01 \quad 0.01$$

A^+ is almost completely hydrolysed, acting as very strong acid, with $K_h > 1$

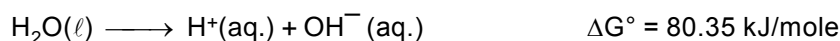
$$\Rightarrow \frac{10^{-14}}{K_b} > 1 \quad \Rightarrow \quad K_b < 10^{-14}$$

10. $10.8 \times 10^{-9} = (0.5S \times 2)^2 (0.5S) \quad \Rightarrow \quad S^3 = \frac{10.8 \times 10^{-9}}{0.25 \times 0.5}$

11. Cell reaction



Also we have



Hence for cell reaction

$$\Delta G^\circ = -96.50 \text{ kJ/mole} \quad \text{So, } E^\circ = -\frac{\Delta G^\circ}{nF} = \frac{96500}{2 \times 96500} = 0.50 \text{ V}$$

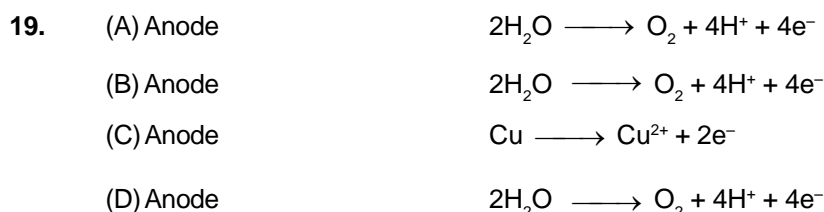
12. The cell is concentration cell So, $E_{\text{cell}} = \frac{-0.059}{1} \log \frac{[\text{Cl}^-]_{\text{cathode}}}{[\text{Cl}^-]_{\text{anode}}}$

more is the difference in concentration of Cl^- in the electrodes, larger is the value of E_{cell} . Hg_2Cl_2 provides least concentration of Cl^- .

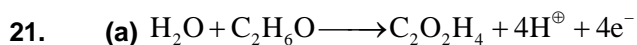
15. According to this graph, \wedge_m first decreases, and after point, \wedge_m is nearly constant.

This happens when HCOOH is added to NaOH , OH^- are removed from solution and HCOO^- replace them. But conductivity of OH^- is very high. Hence conductance keeps on decreasing till the end point. After the endpoint, solution already contain HCOO^- . Hence HCOOH , being weak acid sees common ion effect and do not dissociate much to increase \wedge_m .

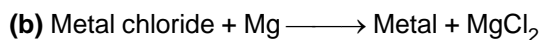
17. $\text{BOH} \rightleftharpoons \text{B}^+ + \text{OH}^-$
as $V \uparrow \propto \uparrow$ so $[\text{OH}^-]$ will decrease $\text{pOH} \uparrow \Rightarrow \text{pH} \downarrow$.



20. Resistance of cell is not due to vibrations of ion but actually it is due to collisions of ions.



'a' = 6



From reaction, 24g of Mg metal produces 95g of MgCl_2

\therefore 9.6g of Mg metal produces $\frac{9.6 \times 95}{24} = 38\text{g}$ of MgCl_2

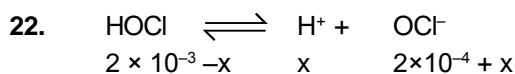
Mass of Cl in MgCl_2 = Mass of Cl in metal chloride = $38 - 9.6 = 28.4\text{g}$

Mass of metal in metal chloride = $52.4 - 28.4 = 24\text{g}$

Now, 28.4g of chlorine combines with 24g of metal

& 35.5g of chlorine combines with Eq Wt of metal (by definition)

\therefore Eq wt. of metal = $\frac{35.5 \times 24}{28.4} = 30 = \text{'b'}$.



$1.5 \times 10^{-4} = \frac{x(2 \times 10^{-4} + x)}{(2 \times 10^{-3} - x)} \quad ; \quad 3 \times 10^{-7} - 1.5 \times 10^{-4}x = 2 \times 10^{-4}x + x^2$

$x^2 + 3.5 \times 10^{-4}x - 3 \times 10^{-7} = 0 \quad ; \quad x = \frac{-3.5 \times 10^{-4} + \sqrt{(3.5 \times 10^{-4})^2 + 12 \times 10^{-7}}}{2} = 4 \times 10^{-4}$

23. Let $m_c = 3x$ and $m_o = 2x \Rightarrow n_c = \frac{3x}{12}$ and $n_o = \frac{2x}{16}$

$= \frac{x}{4} \quad = \frac{x}{8}$

$\Rightarrow n_c ; n_o = \frac{x}{4} : \frac{x}{8} = 2 : 1$

Let the empirical formula be $\text{C}_2\text{H}_x\text{O}$

$x = \frac{66.67}{100} (2 + 1 + x) \quad ; \quad x = \frac{2}{3} (3 + x) \quad ; \quad 3x = 6 + 2x$

$x = 6$

Hence EF = $\text{C}_2\text{H}_6\text{O}$

Molar mass = 2×23

= 46

E. F. mass = $24 + 6 + 16 = 46$

\Rightarrow Molecular formula = $\text{C}_2\text{H}_6\text{O}$

Hence, total number of atoms = $2 + 6 + 1 = 9$

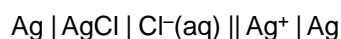
24. (i) On discharging, it generates electricity and hence works as galvanic cell.

(ii) Anode is positively charged during charging

(iii) It depends on the species getting oxidised and reduced.

(iv) E_{cell} depends on temperature

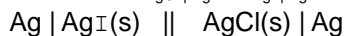
(v) This is true. Example $\text{Ag}^+ + \text{Cl}^- \longrightarrow \text{AgCl}$, is the overall reaction occurring in the cell



(v) It is E_{cell} which determines spontaneity

25. $\text{Ag} | \text{AgCl(s)} || \text{Calomel} \quad E_1$
Saturated solution
 $\text{Ag} | \text{AgI(s)} || \text{Calomel} \quad E_2$
Saturated solution

$$E_2 - E_1 = E_{\text{AgCl} | \text{Ag}} - E_{\text{AgI} | \text{Ag}} = 0.177 \quad ; \quad \text{This can be understood as}$$



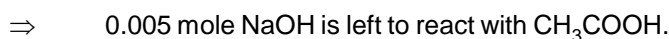
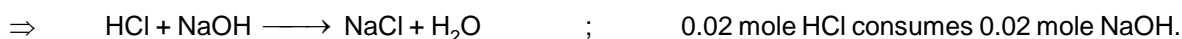
Or



$$\left(\sqrt{K_{sp}(\text{AgI})} \right) \quad \left(\sqrt{K_{sp}(\text{AgCl})} \right)$$

$$\Rightarrow \quad 0.177 = \frac{-0.059 \log [\text{Ag}^+]_a}{1 [\text{Ag}^+]_c} \quad \Rightarrow \quad 0.177 = 0.059 \log \frac{\sqrt{K_{sp}(\text{AgCl})}}{\sqrt{K_{sp}(\text{AgI})}} \quad ; \quad \frac{K_{sp}(\text{AgCl})}{K_{sp}(\text{AgI})} = 10^6$$

26. $n_{\text{CH}_3\text{COOH}} = 0.2 \times 0.1 = 0.02 \quad ; \quad n_{\text{HCl}} = 0.2 \times 0.1 = 0.2 \quad ; \quad n_{\text{NaOH}} = \frac{1}{40} = 0.025$



	0.02	0.005	
left	0.015	0	0.005

The final solution is a buffer.

$$\Rightarrow \quad K_a = \frac{[\text{H}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad \Rightarrow \quad [\text{H}^+] = \frac{K_a \times [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} = \frac{2 \times 10^{-5} \times 0.015}{0.005} = 6 \times 10^{-5}$$

$$x = 6$$

$$y = 5$$

$$\Rightarrow \quad x + y = 11$$

27. $\text{CHCl}_2\text{COOH} \longrightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{Cl}_2$

$$\text{v.f.} = 6$$

$$\Rightarrow \quad \text{moles of } \text{CHCl}_2\text{COOH} \times 6 = 300 \quad \Rightarrow \quad \text{moles of } \text{CHCl}_2\text{COOH} = 50$$

$$\Rightarrow \quad 2\text{CHCl}_2\text{COOH} + \text{Ba(OH)}_2 \rightarrow \text{Ba(CHCl}_2\text{COO)}_2 + 2\text{H}_2\text{O} \quad \Rightarrow \quad n_{\text{Ba(OH)}_2} = \frac{50}{2} = 25$$

28. Molar mass of methanol (CH_3OH) = $32 \text{ g mol}^{-1} = 0.032 \text{ kg mol}^{-1}$

$$\text{Molarity of the given solution} = \frac{0.793 \text{ kg L}^{-1}}{0.032 \text{ kg mol}^{-1}} = 24.78 \text{ mol L}^{-1}$$

Applying

$$M_1 \times V_1 = M_2 V_2$$

$$(\text{Given solution}) \quad (\text{solution to be prepared}) \quad ; \quad 24.78 \times V_1 = 0.22 \times 2.7 \text{ L}$$

$$\text{or} \quad V_1 = 0.024 \text{ L} = 24 \text{ mL}$$





Equivalents at cathode = Equivalents at anode

$$\Rightarrow \frac{10.304}{22.4} \times 2 = \frac{2.24}{22.4} \times 4 + n_{\text{S}_2\text{O}_8^{2-}} \times 2$$

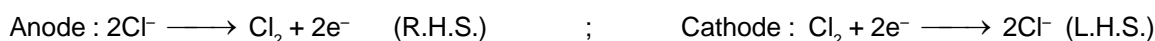
$$\Rightarrow \frac{10.304}{22.4} = \frac{2.24}{22.4} + n_{\text{S}_2\text{O}_8^{2-}} \quad \Rightarrow \quad n_{\text{S}_2\text{O}_8^{2-}} = 0.46 - 0.2 = 0.26$$

$$\Rightarrow m_{\text{S}_2\text{O}_8^{2-}} = 0.26 \times 194 = 50.44$$

$$\approx 50$$

30. Since v.f. of I_2 in both reactions is different, so modification should be applied while applying law of equivalence.

32. $\text{Pt}, \text{Cl}_2 | \text{Cl}^- (\text{aq}) || \text{Cl}^- (\text{aq}) | \text{Cl}_2 (\text{g}), \text{Pt}.$



$$E_{\text{cell}} = 0 - \frac{RT}{nF} \ln \frac{[\text{Cl}^-]_{\text{L.H.S.}}}{[\text{Cl}^-]_{\text{R.H.S.}}} \quad ; \quad E_{\text{cell}} = \frac{RT}{nF} \ln \frac{[\text{Cl}^-]_{\text{R.H.S.}}}{[\text{Cl}^-]_{\text{L.H.S.}}}$$

35. $N_1V_1 + N_2V_2 = N_3V_3$

$$\frac{2.8}{5.6} \times 2 + \frac{16.8}{5.6} \times 2 = \frac{2.55}{34} \times 2 \times V_3 \times 10 \quad \therefore V_3 = \frac{14}{3} \quad \therefore V_w = \frac{14}{3} - 4 = \frac{2}{3} = 0.67\text{L}.$$

36. If max. volume of hypo solution is to be consumed, max. amount of I_2 should be liberated for which the amount of 12.6 V H_2O_2 solution prepared should be maximum.

Now, max. volume of 12.6 V H_2O_2 solution can be prepared by using 16.8 V H_2O_2 solution completely (2 L) and 2.8 V H_2O_2 solution partially (< 2 L).

$$\therefore M_1V_1 + M_2V_2 = M_fV_f \quad \therefore \left(\frac{16.8}{11.2} \times 2 \right) + \left(\frac{2.8}{11.2} \times V \right) = \frac{12.6}{11.2} \times (2 + V)$$

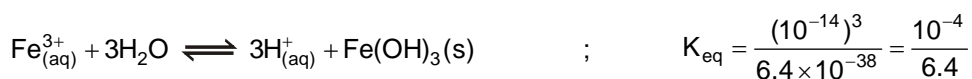
Upon solving, $V = \frac{6}{7} \text{ L}.$

$$\therefore \text{Max. volume of 12.6 V } \text{H}_2\text{O}_2 \text{ sol} = 2 + V = \frac{20}{7} \text{ L}.$$

Now, $\text{eq}_{\text{H}_2\text{O}_2} = \text{eq}_{\text{Hypo}}$

$$\left(\frac{12.6}{5.6} \times \frac{20}{7} \right) = \frac{9}{7} \times V_{\text{Hypo}} \quad \therefore V_{\text{Hypo}} = 5 \text{ L}.$$

37. $\text{Fe}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Fe}^{3+}(\text{aq}) + 3\text{OH}^{-}(\text{aq})$ 6.4×10^{-38} (1)
 $\text{H}_2\text{O} \rightleftharpoons \text{H}^{+} + \text{OH}^{-}$ 10^{-14} (2)
 Doing 3×-1



38. $\text{Fe}^{3+} + \text{Al}(\text{OH})_3(\text{s}) \rightleftharpoons \text{Fe}(\text{OH})_3(\text{s}) + \text{Al}^{3+}$

$$K_{\text{eq}} = \frac{2 \times 10^{-33}}{6.4 \times 10^{-38}} = \frac{1 \times 10^5}{3.2} \quad ; \quad \text{The large } K_{\text{eq}} \text{ suggest, red particles of } \text{Fe}(\text{OH})_3 \text{ will precipitate}$$

39. Water already contains $[\text{OH}^{-}] = 10^{-7}$ which exert common ion effect on solubility of $\text{Fe}(\text{OH})_3$.

To avoid precipitation ;

$$Q_{\text{SP}} = K_{\text{sp}}$$

Let $[\text{Fe}_2(\text{SO}_4)_3] = x$

$$\Rightarrow [\text{Fe}^{3+}] = 2x \quad \Rightarrow 2x \times (10^{-7})^3 = 6.4 \times 10^{-38} \quad \Rightarrow 2x \times 10^{-21} = 6.4 \times 10^{-38}$$

$$\Rightarrow x = 3.2 \times 10^{-17} \quad \Rightarrow n_{\text{Fe}_2(\text{SO}_4)_3} \text{ in 2 L water} = 6.4 \times 10^{-17}$$

40. Cathode : $\text{NO}_3^{-} + 3\text{H}_3\text{O}^{+} + 2\text{e}^{-} \longrightarrow \text{HNO}_2 + 4\text{H}_2\text{O}$; $E^{\circ} = 0.94 \text{ V}$

- Anode : $2\text{Hg}^{2+} + 2\text{e}^{-} \longrightarrow \text{Hg}_2^{2+}$; $E^{\circ} = 0.92 \text{ V}$

Overall balanced cell reaction :



$$E = E^{\circ}_{\text{cell}} - \frac{0.06}{2} \log \frac{[\text{Hg}^{2+}]^2 [\text{HNO}_2]}{[\text{NO}_3^{-}] [\text{H}_3\text{O}^{+}]^3 [\text{Hg}_2^{2+}]}$$

$$E = E^{\circ}_{\text{cell}} - \frac{0.06}{2} \log \frac{1}{[\text{H}_3\text{O}^{+}]^3}$$

$$0 = 0.02 - 0.03 \log \frac{1}{[\text{H}_3\text{O}^{+}]^3}$$

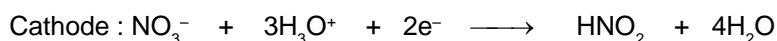
$$0 = 0.02 - 0.03 \times 3 (\text{pH})$$

$$\text{pH} = \frac{0.02}{0.03 \times 3} = \left(\frac{2}{9} \right).$$

41. $\text{NO}_3^{-} + 3\text{H}_3\text{O}^{+} + \text{Hg}_2^{2+} \longrightarrow 2\text{Hg}^{2+} + \text{HNO}_2 + 4\text{H}_2\text{O}$

$$t = 0 \quad 0.4 \quad - \quad 0.5 \quad - \quad - \quad -$$

$$t = t \quad 0.1 \text{mole} \quad - \quad 0.2 \text{mole} \quad 0.6 \text{mole} \quad 0.3 \text{mole} \quad -$$



$$0.6 \text{mole} \quad 0.3 \text{mole}$$



42. (A) $[\text{Cl}^-] = \frac{50 \times 3 + 150 \times 1 \times 3}{200} = \frac{600}{200} = 3 \text{ M}$

(B) molality = $\frac{0.1}{0.9 \times 18} \times 1000 = 6.17 \text{ m}$

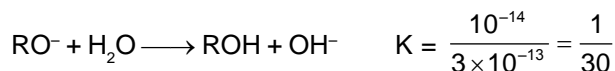
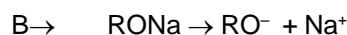
(C) Molality = $\frac{10 \times 1000}{60 \times 90} = 1.85 \text{ m}$.

(D) Molarity of HCl = $\frac{\frac{10.95}{36.5}}{100} \times 1000 = 3 \text{ M}$

43. A → given in qn 9

B → $\text{pH} = \frac{\text{p}K_1 + \text{p}K_2}{2} = \frac{7 - \log 4 + 11 - \log 4}{2} = 9 - 2 \log 2$
 $= 9 - 0.6$
 $= 8.4$

C → $[\text{H}^+] = \sqrt{K_1 \times C + K_w}$
 $= \sqrt{3 \times 10^{-13} \times 0.1 + 10^{-14}} = 2 \times 10^{-7}$
 $\text{pH} = 7 - \log 2 = 6.7$



At eq. $10^{-3} - x \quad x \quad x$

$\frac{x^2}{10^{-3} - x} = \frac{1}{30} \Rightarrow x = 10^{-3} \Rightarrow \text{H}^+ = 10^{-11}, \text{pH} = 11$

$\text{vf} = 3 \quad \text{vf} = 6$

44. (A) For AgBr, $K_{\text{sp}} = [\text{Ag}^+][\text{Br}^-]$
 so on increase in $[\text{Br}^-]$, solubility of AgBr decreases.
- (B) For AgCN, $K_{\text{sp}} = [\text{Ag}^+][\text{CN}^-]$
 CN^- undergoes hydrolysis so solubility in water is more than expectation.
 In acidic solution, CN^- gets protonated so solubility of AgCN increases.
 AgCN forms complex $\text{Ag}(\text{CN})_2^-$ with excess of CN^- .
- (C) For $\text{Fe}(\text{OH})_3$, $K_{\text{sp}} = [\text{Fe}^{3+}][\text{OH}^-]^3$.
 In acidic solution OH^- decreases so solubility increases.
 Solubility decreases in presence of OH^- .
- (D) For $\text{Zn}(\text{OH})_2$, $K_{\text{sp}} = [\text{Zn}^{2+}][\text{OH}^-]^2$
 $\text{Zn}(\text{OH})_2$ is amphoteric in nature so its solubility increases in both acidic as well as strongly basic solution.

45. (A) Both cathode and anode are Hydrogen electrodes. So, given cell is a concentration cell.

Now, $[\text{OH}^-]_a = 0.01 \text{ M}$

$\therefore [\text{H}^+]_a = 10^{-12} \text{ M}$ and $[\text{H}^+]_c = 10^{-2} \text{ M}$

So,
$$E_{\text{cell}} = -\frac{0.059}{1} \log_{10} \frac{[\text{H}^+]_a}{[\text{H}^+]_c} = -0.059 \times (-10) = 0.59 \text{ V } (> 0)$$

(B)
$$E_{\text{cell}} = [E^\circ_{\text{Ag}^+/\text{Ag}} - E^\circ_{\text{Zn}^{2+}/\text{Zn}}] - \frac{0.059}{2} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2}$$

$$= 1.57 - \frac{0.059}{2} \log_{10} 10 (> 0)$$

(C)
$$E_{\text{cell}} = [E^\circ_{\text{H}^+/\text{H}_2} - E^\circ_{\text{D}^+/\text{D}_2}] - \frac{0.059}{2} \log_{10} \left(\frac{[\text{D}^+]^2 \times p_{\text{H}_2}}{[\text{H}^+]^2 \times p_{\text{D}_2}} \right)$$

$$= 0 - (-0.01) - \frac{0.059}{2} \log_{10} \left(\frac{(0.1)^2 \times 0.001}{(0.01)^2 \times 0.1} \right)$$

$$= 0.01 \text{ V } (> 0)$$

Since the expression of log upon solving has value 1, so, $E_{\text{cell}} = E^\circ_{\text{cell}}$ and it can be said that Cell will have the same emf as the one made up of standard electrodes.

Also the expression of log will have the same value even after diluting each electrode solution to double volume. So, it would not affect emf of cell.

(D)
$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.059}{1} \log_{10} \frac{[\text{Cl}^-]}{[\text{Br}^-]}$$

$$= \frac{0.059}{1} \log_{10} \frac{K_{\text{sp}} [\text{AgCl}]}{K_{\text{sp}} [\text{AgBr}]} - \frac{0.059}{1} \log_{10} \frac{[\text{Cl}^-]}{[\text{Br}^-]}$$

$$= \frac{0.059}{1} \log_{10} \frac{(10^{-10})}{(5 \times 10^{-13})} - \frac{0.059}{1} \log_{10} \frac{(0.1)}{(5 \times 10^{-4})}$$

$$= 0$$

So, cell reaction is at equilibrium.

Also, upon diluting the electrode solutions to double volume, both E°_{cell} and expression of log will remain unchanged. So, E_{cell} will remain zero and thus, no change in emf of cell would occur.