Consider hydrogen electrode,

$$H^+ + e^- \rightarrow \frac{1}{2}H_2$$

$$E_{H^+|H_2} = E^0_{H^+|H_2} - \frac{0.0591}{n}\log\frac{\left(P_{H_2}\right)^{1/2}}{\left[H^+\right]}$$

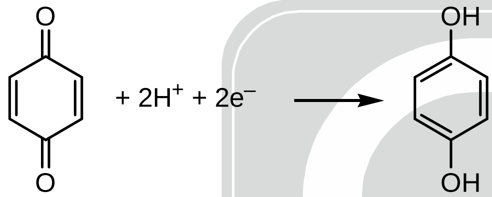
If $P_{H_2} = 1$ bar then,

$$E_{H^+|H_2} = 0 - 0.0591\log\frac{1}{\left[H^+\right]}$$

$$E_{H^+|H_2} = -0.0591\left\{-\log\left[H^+\right]\right\}$$

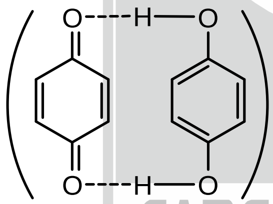
$$E_{H^+|H_2} = -0.0591\,pH$$

$\rightarrow$ **Quinhydrone Electrode :-** $Q, QH_2, H^+ | Au$



$$Q + 2H^+ + 2e^- \rightarrow QH_2$$

Quinone Hydroquinone

Quinhydrone  is slightly soluble in water releasing quinone and hydroquinone in the same amount.

$$Q + 2H^+ + 2e^- \rightarrow QH_2$$

$$E = E^0 - \frac{0.0591}{2}\log\frac{[QH_2]}{[Q]\left[H^+\right]^2}$$

$$E = E^0 - \frac{0.0591}{2}\left\{-\log\left[H^+\right]^2\right\}\left([Q] = [QH_2]\right)$$

$$E = E^0 - 0.0591\,pH\,; \quad E^0_{Q,QH_2,\,H^+|Au} = 0.6996\text{ V}$$

Problem: The cell pontential for the following electrochemical system at 25ºC is:

$$Al(s)\,|\,Al^{3+}(0.01\text{ M})\,\|\,Fe^{2+}(0.1\text{ M})\,|\,Fe(s)$$

(a) 1.23 V (b) 1.21 V (c) 1.22 V (d) –2.10 V

Given : Standard reduction potential of $Al^{3+} + 3e^- \rightarrow Al$ is -1.66 V at 25° C

Standard reduction potential of $Fe^{2+} + 2e^- \rightarrow Fe$ is -0.44 V at 25° C

Soln. Net cell reaction :- $2Al(s) + 3Fe^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Fe(s)$

$$E = E^0_{cell} - \frac{0.0591}{6}\log\frac{[Al^{3+}]^2}{[Fe^{2+}]^3}$$

$$= [-0.44-(-1.66)] - \frac{0.0591}{6}\log\frac{(10^{-2})^2}{(10^{-1})^3}$$

$$E = 1.22 - \frac{0.0591}{6}\log 10^{-1}$$

$$E = 1.22 + \frac{0.0591}{6} = 1.229 \simeq 1.23\ \text{V}$$

Correct option is (a)

Problem: According to the Nernst equation, the potential of an electrode changes by 59.2 mV whenever the ratio of the oxidized and the reduced species changes by a factor of 10 at 25ºC. What would be the corresponding change in the electrode potential if the experiment is carried out at 30ºC ?

(a) 59.2 mV (b) 71.0 mV (c) 60.2 mV (d) None of the above

Soln. $M^{n+} + ne^- \longrightarrow M$

At 298 K,

$$E_1 = E^0 - \frac{0.0591}{n}\log\frac{[\text{Reduced}]}{[\text{Oxidised}]}$$

On changing the ratio by factor 10

$$E_2 = E^0 - \frac{0.0591}{n}\log 10\frac{[\text{Reduced}]}{[\text{Oxidised}]}$$

$$= E^0 - \frac{0.0591}{n}\log\frac{[\text{Reduced}]}{(\text{Oxidation})} - \frac{0.0591}{n}\log 10$$

$$E_2 = E_1 - \frac{0.0591}{n}$$

or $E_2 - E_1 = \frac{59.1}{n}\text{mV}$

The case taken in the problem has n = 1

$E_2 - E_1 = 59.1\ \text{mV}$

Correct option is (c)

Problem: The standard redox potential of water oxidation to dioxygen is –1.23 V,

$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$

The redox potential of the same reaction at pH = 7 would be :

(a) -0.41 V (b) -1 V (c) -0.82 V (d) -1.64 V

Soln. $2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \quad E = -1.23\ \text{V}$

$$E = E^0 - \frac{0.0591}{n}\log[H^+]^4$$