Experiment-5

Title: *Write a program to compute and plot the E-pH diagam for Aluminum in water at 25°C*

Consider only four species containing aluminum:

- 2 solid species (Al and $Al_2O_3.H_2O$)
- 2 liquid species (Al^{3+} and AlO^{2-})

$$Al^{3+} + 2H_2O \rightleftarrows AlO_2^- + 4H^+$$

Solution:

$$Al^{3+} + 2H_2O \rightleftarrows AlO_2^- + 4H^+$$

There is no change in valence of the aluminum present in the two ionic species considered.

∴ the associated equilibrium is independent of the potential.

The expression of that equilibrium can be derived in the following expression for standard conditions:

$$RT \ln K_{eq} = RT \ln Q = -\Delta G^0_{reaction}$$

where **Q** is expressed is given by the equation

$$Q = \frac{a_{AlO_2^-} \times a_{H^+}^4}{a_{Al^{3+}} \times a_{H_2O}^2}$$

Assuming that the activity of H_2O is unity and that the activities of the two ionic species are equal, one can obtain a simpler expression of the equilibrium in equation based purely on the activity of H^+, and its logarithmic form, equation:

$$RT \ln [H^+]^4 = -\Delta G^0_{reaction}$$

$$\log_{10}[H^+] = -pH = \frac{-\Delta G^0_{reaction}}{4 \times 2.303 \times RT}$$

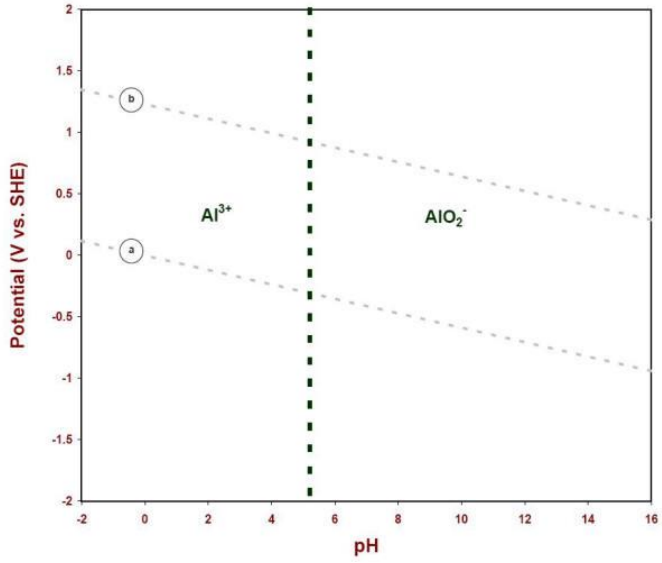
and if $\mathbf{G}^0$ is expressed in Joules and the temperature is 25ºC or 298 K equation is even further simplified.

$$pH = 4.38 \times 10^{-5} \times \Delta G^0_{reaction}$$

By using the standard thermodynamic data from the literature, it is possible to calculate that the free energy of reaction is in fact equal to 120.44 kJ mol^{-1} when both $[Al^{3+}]$ and $[AlO_2^-]$ are equal. Equation then becomes:

$$pH = 4.38 \times 10^{-5} \times 120{,}440 = 5.27$$

This is represented, in the E-pH diagram shown below, by a dotted vertical line separating the dominant presence of Al^{3+} at low pH from the dominant presence of AlO_2^- at the higher end of the pH scale.



E-pH diagram showing the soluble species of aluminum in water at 25ºC

Conclusion:

In the Al-H_2O system, the dominant species is: Al^{3+} ions when the pH is below 5.27 and AlO_2^- ions when the pH is above 5.27