Chapter 8 Activity

Hydrated radius
Ionic atmosphere

Effect on and insoluble salt

Ionic strength (μ)

$\mu = \frac{1}{2} \sum c_i z_i^2$

Example the ionic strength of a solution consisting of 0.100 M KCl and 0.050 M NaCl

Activity – the "perceived" concentration

$$\mathcal{A}_c = [C]\gamma_c$$

Use Activities in place of concentration

$$A + B \leftrightarrow C + D$$

$$K \approx [C][D] / [A][B], \quad K = \mathcal{A}_C \mathcal{A}_D / \mathcal{A}_A \mathcal{A}_D$$

OK! So what is γ? Activity Coefficient

How do you get γ? 2 ways

1. extended debye-Huckle eq: $\log g = -0.51z^2(\mu)^{1/2}/(1+(a*(\mu)^{1/2}/305))$
2. Apply Table 8-1 and extrapolate (suggested)

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$$Hg_2Br_2 \leftrightarrow Hg_2^{2+} + 2Br^-$$

$$Ksp = [Hg_2^{2+}]\gamma_{(Hg22+)} [Br^-]^2\gamma_{(Br-)}^2$$

$$2[Hg_2^{2+}] = [Br^-]$$

so,

$$Ksp = 4\, \gamma_{(Hg22+)} \gamma_{(Br-)}^2 [Hg_2^{2+}]^3$$

a) 0.00100 M KNO_3

$[K^+] = [NO_3^-] = 0.00100$

$\mu = ½[(.001)(+1)^2 + (.001)(-1)^2] = 0.00100$

$\gamma(Hg_2^{2+}$ at $\mu = 0.001$ M$) = 0.867$

$\gamma(Br^-$ at $\mu = 0.001$ M$) = 0.964$

$Ksp \quad = 5.6*10^{-23} = 4\ \gamma_{(Hg22+)}\ \gamma_{(Br-)}^2\ [Hg_2^{2+}]^3$

$[Hg_2^{2+}] \quad = (5.6*10^{-23})/[(4)*(0.867)*(0.964)^2]$
$= 2.6*10^{-8}$ M

b) 0.0100 M KNO_3
$[K^+] = [NO_3^-] = 0.0100$

$\mu = ½[(.01)(+1)^2 + (.01)(-1)^2] = 0.0100$

$\gamma(Hg_2^{2+}$ at $\mu = 0.01$ M$) = 0.660$

$\gamma(Br^-$ at $\mu = 0.01$ M$) = 0.901$

$Ksp \quad = 5.6*10^{-23} = 4\ \gamma_{(Hg22+)}\ \gamma_{(Br-)}^2\ [Hg_2^{2+}]^3$

$[Hg_2^{2+}] \quad = (5.6*10^{-23})/[(4)*(0.660)*(0.901)^2]$
$= 3.0*10^{-8}$ M

c) 0.100 M KNO_3
$[K^+] = [NO_3^-] = 0.100$

$\mu = ½[(.1)(+1)^2 + (.1)(-1)^2] = 0.100$

$\gamma(Hg_2^{2+}$ at $\mu = 0.1$ M$) = 0.355$
$\gamma(Br^-$ at $\mu = 0.1$ M$) = 0.755$

$Ksp \quad = 5.6*10^{-23} = 4\ \gamma_{(Hg22+)}\ \gamma_{(Br-)}^2\ [Hg_2^{2+}]^3$

$[Hg_2^{2+}] \quad = (5.6*10^{-23})/[(4)*(0.355)*(0.755)^2]$
$= 4.1*10^{-8}$ M

Example 8-20

8-20

$\mu = \frac{1}{2}\{[Li^+](+1)^2 + [NO_3^-](-1)^2 + [Na^+](+1)^2 + [OH^-](-1)^2\}$
$= \frac{1}{2}\{(0.012)(+1)^2 + (0.012)(-1)^2 + (0.010)(+1)^2 + (0.010)(-1)^2\}$
$= 0.022$ M

This lies between 0.01 M ($\gamma(OH^-) = 0.900$) and 0.05 M ($\gamma(OH^-) = 0.81$) on Table 8.1. We must extrapolate linearly to obtain $\gamma(OH^-)$ at $\mu = 0.022$ M.

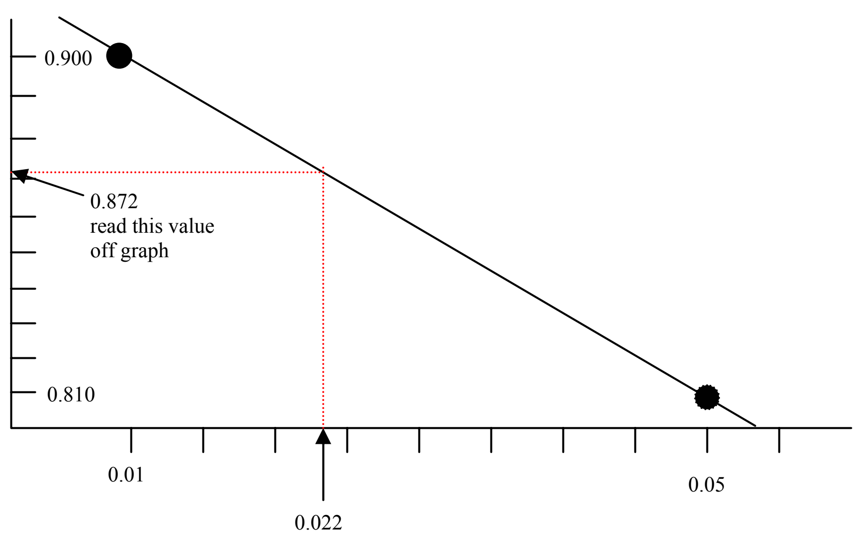
(0.900-x)/(0.900-0.81) = (0.01-0.022)/(0.01–0.05)
0.900-x = ((-0.012)/(-0.04))*(0.09)
x = 0.900 – 0.027 = 0.873

$A_{H+} = [H^+]\gamma_{H+} = Kw/([OH^-]\gamma_{OH-}) = 10^{-14}/[(0.01)*(.873)]$
$= 1.2*10^{-12}$ M

pH = -log A_{H+} = 11.94

without using activity
pH = log$[H^+]$ = 12.00

As an alternative to the above method for finding γ_{OH-} at $\mu = 0.022$ M, you can make a quick graph



9.24

charge balance

$$[OH^-] + [G^-] = [FeG^+] + [H^+]$$

mass balance 1

$$0.1000 = 2[FeG_2] + [FeG^+] + [G^-] + [HG]$$

mass balance 2

$$0.0500 = [FeG_2] + [FeG^+] \rightarrow [FeG_2] = 0.0500 - [FeG^+]$$

$$K_b = [OH^-][HG] / [G^-] \rightarrow [HG] = K_b [G^-]\gamma_{G-} / [OH^-]\gamma_{OH-}$$

$$K_2 = [FeG_2] / [G^-][FeG^+] \rightarrow [G^-] = [FeG_2] / K_2[FeG^+]\gamma_{FeG+}\gamma_{G-}$$

Make substitutions into mass balance 1

$$0.1000 = 2[FeG_2] + [FeG^+] + [G^-] + [HG]$$

$$0.1000 = 2(0.0500 - [FeG^+]) + [FeG^+] + (0.0500 - [FeG^+])/ K_2[FeG^+]\gamma_{FeG+}\gamma_{G-} + (K_b (0.0500 - [FeG^+]) \gamma_{G-})/(K_2[OH^-] \gamma_{OH-} [FeG^+]\gamma_{FeG+}\gamma_{G-})$$

Successive approx with excel

$[FeG^+] = 0.0811$ M
without activity coefficients
$[FeG^+] = 0.01476$ M