

Chapter 7 Homework

- 7-5.** The ionic strength 0.030 M is halfway between the values 0.01 and 0.05 M. Therefore, the activity coefficient will be halfway between the tabulated values:

$$\gamma = \frac{1}{2}(0.914 + 0.86) = 0.887.$$

7-6. (a) $\log \gamma = \frac{-0.51 \cdot 2^2 \cdot \sqrt{0.083}}{1 + (600\sqrt{0.083} / 305)} = -0.375 \Rightarrow \gamma = 10^{-0.375} = 0.422$

(b) $\gamma = \left(\frac{0.083 - 0.05}{0.1 - 0.05}\right)(0.405 - 0.485) + 0.485 = 0.432$

- 7-9.** The solubility of Hg_2Br_2 is small, so we assume that Hg_2Br_2 contributes negligible Br^- to 0.001 00 M KBr.

$$\mu = 0.001 \text{ 00 M}, [\text{Br}^-] = 0.001 \text{ 00 M}, \gamma_{\text{Hg}_2^{2+}} = 0.867, \gamma_{\text{Br}^-} = 0.964$$

$$\begin{aligned} K_{\text{sp}} &= 5.6 \times 10^{-23} = [\text{Hg}_2^{2+}] \gamma_{\text{Hg}_2^{2+}} [\text{Br}^-]^2 \gamma_{\text{Br}^-}^2 \\ &= [\text{Hg}_2^{2+}] (0.867) (0.001 \text{ 00})^2 (0.964)^2 \Rightarrow [\text{Hg}_2^{2+}] = 7.0 \times 10^{-17} \text{ M} \end{aligned}$$

Check our assumption: Yes, Br^- from Hg_2Br_2 is negligible.

- 7-10.** The solubility of $\text{Ba}(\text{IO}_3)_2$ is small, so we assume that $\text{Ba}(\text{IO}_3)_2$ contributes negligible IO_3^- to 0.100 M $(\text{CH}_3)_4\text{NIO}_3$.

$$\mu = 0.100 \text{ M}, [\text{IO}_3^-] = 0.100 \text{ M}, \gamma_{\text{Ba}^{2+}} = 0.38, \gamma_{\text{IO}_3^-} = 0.775$$

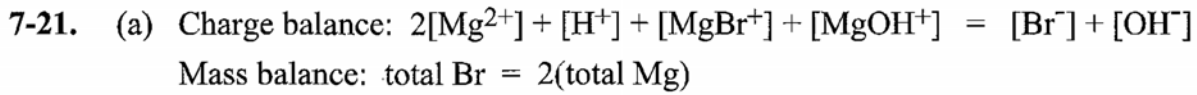
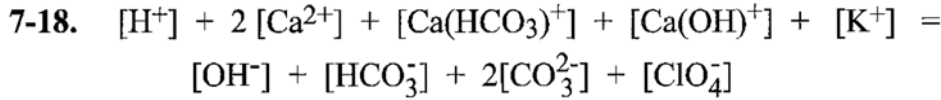
$$\begin{aligned} K_{\text{sp}} &= 1.5 \times 10^{-9} = [\text{Ba}^{2+}] \gamma_{\text{Ba}^{2+}} [\text{IO}_3^-]^2 \gamma_{\text{IO}_3^-}^2 \\ &= [\text{Ba}^{2+}] (0.38) (0.100)^2 (0.775)^2 \Rightarrow [\text{Ba}^{2+}] = 6.6 \times 10^{-7} \text{ M} \end{aligned}$$

- 7-12.** Ionic strength = 0.010 M from NaOH + 0.012 M from LiNO_3 = 0.022 M. Interpolating in Table 7-1 gives $\gamma_{\text{OH}^-} = 0.873$.

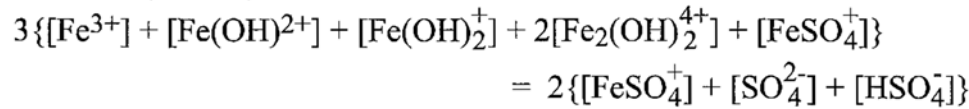
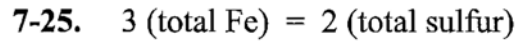
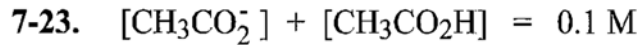
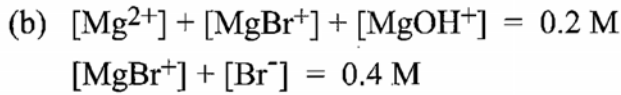
$$[\text{H}^+] \gamma_{\text{H}^+} = \frac{K_w}{[\text{OH}^-] \gamma_{\text{OH}^-}} = \frac{1.0 \times 10^{-14}}{(0.010)(0.873)} = 1.15 \times 10^{-12}$$

$$\text{pH} = -\log(1.15 \times 10^{-12}) = 11.94$$

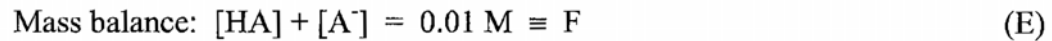
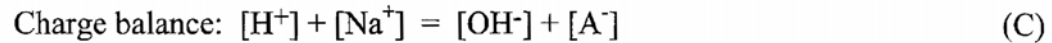
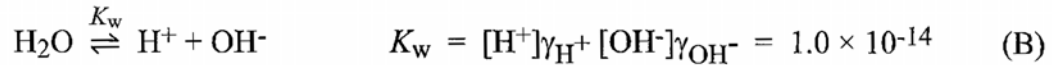
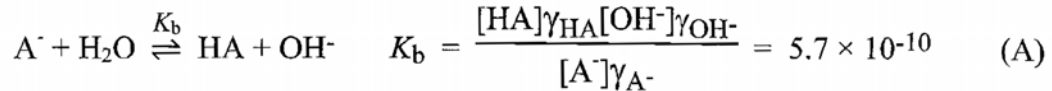
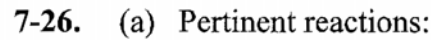
If we had neglected activities, $\text{pH} \approx -\log[\text{H}^+] = -\log \frac{K_w}{[\text{OH}^-]} = 12.00$



$$[MgBr^+] + [Br^-] = 2\{[Mg^{2+}] + [MgBr^+] + [MgOH^+]\}$$



We write 2 in front of $[Fe_2(OH)_2^{4+}]$ because $Fe_2(OH)_2^{4+}$ contains 2 Fe.



(b) Now we neglect activity coefficients. We will make the following substitutions in the charge balance:

$$[OH^-] = K_w/[H^+]$$

$$\text{From Equation A: } [HA] = \frac{K_b[A^-]}{[OH^-]} \quad (F)$$

$$\text{From Equation E: } [HA] = F - [A^-] \quad (G)$$

Now equate the expressions for [HA] from Equations F and G to solve for [A⁻]

$$\frac{K_b[A^-]}{[OH^-]} = F - [A^-]$$

$$[A^-] \left(\frac{K_b}{[OH^-]} + 1 \right) = F \Rightarrow [A^-] = \frac{F[OH^-]}{K_b + [OH^-]}$$

Now substitute $K_w/[H^+]$ for each $[OH^-]$ in the equation above to get

$$[A^-] = \frac{FK_w/[H^+]}{K_b + K_w/[H^+]} = \frac{FK_w}{K_b[H^+] + K_w} \quad (H)$$

We can now substitute for all terms in the charge balance using $[A^-]$ from Equation H, $[OH^-] = K_w/[H^+]$, and $[Na^+] = F$:

Charge balance: $[H^+] + [Na^+] = [OH^-] + [A^-]$

$$[H^+] + F = \frac{K_w}{[H^+]} + \frac{FK_w}{K_b[H^+] + K_w} \quad (I)$$

Equation I has the form we were looking for. The only unknown is $[H^+]$. For convenience in finding a numerical solution, I will rearrange as follows:

$$0 = \frac{K_w}{[H^+]} + \frac{FK_w}{K_b[H^+] + K_w} - [H^+] - F \quad (J)$$

The following spreadsheet evaluates the right side of Equation J in cell D9.

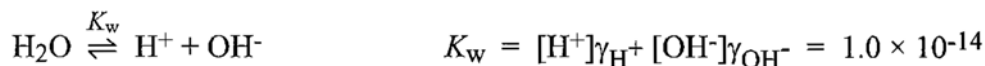
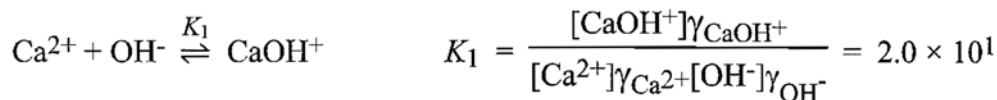
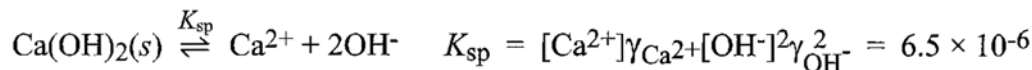
Guess a value for $[H^+]$ in cell B7. Before using Goal Seek in Excel 2007, click the Microsoft Office button at the top left of the spreadsheet, click on Excel Options, and then on Formulas. Set Maximum Change to $1e-14$. In earlier versions of Excel, go to Tools and Options and select the Calculations tab and set Maximum change to $1e-14$. Then execute Goal Seek to vary $[H^+]$ in cell B7 until the sum in cell D9 is close to 0 (within $1e-14$). The answer in cell B7 is $[H^+] = 4.19 \times 10^{-9}$ M or $pH = 8.38$.

Cells C15:C17 compute other concentrations from the relations

$$[OH^-] = \frac{K_w}{[H^+]} \quad [A^-] = \frac{FK_w}{K_b[H^+] + K_w} \quad [HA] = \frac{K_b[A^-]}{[OH^-]}$$

	A	B	C	D	E
1	Finding the species in NaOAc solution				
2	Using GOAL SEEK to Solve for $[H^+]$				
3	$K_w =$	1.00E-14			
4	$K_b =$	5.70E-10			
5	$F =$	0.01			
6					
7	Guess for $[H^+] =$	4.19E-09		$pH = -\log[H^+] =$	8.38
8					
9	$K_w/[H^+] + FK_w/(K_b[H^+] + K_w) - [H^+] - F =$			4.41E-16	
10					
11	Tools --> Options --> Calculation --> Maximum change = $1e-14$				
12	Use GOAL SEEK to vary $[H^+]$ in cell B7 until the sum in				
13	cell D9 is equal to zero				
14					
15	$[OH^-] = K_w/[H^+] =$		2.39E-06		
16	$[A^-] = FK_w/(K_b[H^+] + K_w) =$		1.00E-02		
17	$[HA] = K_b[A^-]/[OH^-] =$		2.39E-06		

7-27. (a) Pertinent reactions:



$$\text{Charge balance: } 2[\text{Ca}^{2+}] + [\text{CaOH}^+] + [\text{H}^+] = [\text{OH}^-]$$

$$\text{Mass balance: } \underbrace{[\text{OH}^-] + [\text{CaOH}^+]}_{\text{species containing OH}^-} = 2 \underbrace{\{[\text{Ca}^{2+}] + [\text{CaOH}^+]\}}_{\text{species containing Ca}^{2+}} + [\text{H}^+]$$

species containing OH⁻ species containing Ca²⁺

(Mass balance gives the same result as charge balance.)

There are 4 equations (3 equilibria and charge balance) and 4 unknowns:

[Ca²⁺], [CaOH⁺], [H⁺], and [OH⁻].

(b) The approximations we make are to disregard the activity coefficients and to neglect [H⁺] in the charge balance because [H⁺] << [OH⁻] in basic solution.

The charge balance becomes

$$2[\text{Ca}^{2+}] + [\text{CaOH}^+] = [\text{OH}^-] \quad (\text{A})$$

Substituting [CaOH⁺] = K₁[Ca²⁺][OH⁻] into (A) gives

$$2[\text{Ca}^{2+}] + K_1[\text{Ca}^{2+}][\text{OH}^-] = [\text{OH}^-] \Rightarrow [\text{Ca}^{2+}] = \frac{[\text{OH}^-]}{2 + K_1[\text{OH}^-]}$$

Substitute this expression for [Ca²⁺] into the solubility product:

$$K_{sp} = [\text{Ca}^{2+}][\text{OH}^-]^2 = \frac{[\text{OH}^-]^3}{2 + K_1[\text{OH}^-]} \quad (\text{B})$$

We solve Equation B in the spreadsheet by guessing $[\text{OH}^-]$ in cell C4 until the expression in cell D4 is equal to K_{sp} . We used Goal Seek for this purpose.

	A	B	C	D
1	Ca(OH) ₂ solubility			
2				
3	$K_{\text{sp}} =$		$[\text{OH}^-]_{\text{guess}} =$	$[\text{OH}^-]^3 / (2 + K_1[\text{OH}^-]) =$
4	6.5E-06		0.0253528	6.5000E-06
5	$K_1 =$			
6	2.0E+01		$[\text{Ca}^{2+}] =$	$[\text{CaOH}^+] =$
7			0.0101126	0.0051276
8				
9	$D4 = C4^3 / (2 + A6 * C4)$			$[\text{H}^+] = K_w / [\text{OH}^-] =$
10	$C7 = A4 / C4^2$			3.94E-13
11	$D7 = A6 * C7 * C4$			

Results: $[\text{Ca}^{2+}] = 0.010 \text{ M}$ $[\text{CaOH}^+] = 0.005 \text{ M}$
 $[\text{OH}^-] = 0.025 \text{ M}$ $[\text{H}^+] = K_w / [\text{OH}^-] = 3.9 \times 10^{-13} \text{ M}$

Total dissolved Ca = $0.010 \text{ M} + 0.005 \text{ M} = 0.015 \text{ M}$

The formula mass of Ca(OH)₂ is 74.09 g/mol, so 0.015 M is 1.1₃ g/L. The *Handbook of Chemistry and Physics* lists the solubility of Ca(OH)₂ as 1.85 g/L at 0°C and 0.77 g/L at 100°C.