

Part I (48 points). Show your work on problems. Write the relevant equilibrium reactions and corresponding equilibrium constant expressions where appropriate. Evaluation based on correctness, completeness and clarity. Use appropriate number of significant figures in final result. Take activity coefficients into account except as noted.

Equilibrium constants at zero ionic strength

Ba(IO ₃) ₂	K _{sp} = 1.57 × 10 ⁻⁹
PbI ₂	K _{sp} = 7.9 × 10 ⁻⁹
HIO ₃	K _a = 0.17

Activity Coefficients

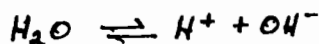
Ion	Ionic Strength	
	0.05	0.10
K ⁺ , NO ₃ ⁻ , OH ⁻	0.81	0.75
Pb ²⁺	0.45	0.36
I ⁻	0.81	0.75
H ⁺	0.85	0.83

For a weak acid HA, $\alpha_{HA} = \frac{[H^+]}{\frac{[H^+]}{K_a} + 1}$ $\alpha_{A^-} = \frac{1}{\frac{[H^+]}{K_a} + 1}$

1. (12) Consider an aqueous solution of 0.10 M NaCl with no added acid or base.
 a) What is the ionic strength of the solution?

$\mu = 0.10$

- b) Develop an expression for K_w', the conditional ionization constant for water, and calculate its value.



$K_w^0 = (a_{H^+})(a_{OH^-}) = \gamma_{H^+} \gamma_{OH^-} [H^+][OH^-] = \gamma_{H^+} \gamma_{OH^-} K_w'$

$K_w' = \frac{K_w^0}{\gamma_{H^+} \gamma_{OH^-}} = \frac{1.00 \times 10^{-14}}{(0.83)(0.75)} = 1.61 \times 10^{-14}$

- c) Calculate the pH of the solution.

$K_w' = [H^+][OH^-] = [H^+]^2$

$[H^+] = \sqrt{K_w'} = \sqrt{1.61 \times 10^{-14}} = 1.27 \times 10^{-7} \text{ M}$

$a_{H^+} = \gamma_{H^+} [H^+] = (0.83)(1.27 \times 10^{-7}) = 1.05 \times 10^{-7}$

$pH = -\log a_{H^+} = -\log(1.05 \times 10^{-7}) = \cancel{6.98} 6.978 \approx 6.98$

2. (4) Calculate the ionic strength of 0.010 M K_2SO_4 .

$$K_2SO_4 \rightarrow \underset{0.020}{2K^+} + \underset{0.010}{SO_4^{2-}}$$

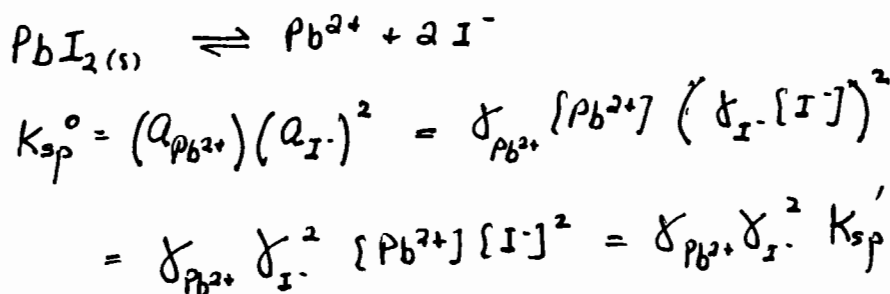
$$\mu = \frac{1}{2} \{ [K^+] (+1)^2 + [SO_4^{2-}] (-2)^2 \}$$

$$= \frac{1}{2} \{ (0.020)(1)^2 + (0.010)(4) \}$$

$$= \frac{1}{2} \{ 0.020 + 0.040 \} = \frac{1}{2} (0.060) = 0.030$$

3. (12) Consider a saturated aqueous solution of PbI_2 in 0.10 M KNO_3 and 0.00100 M KI . Take activity coefficients into account in responding to the following questions.

- a) Beginning with the equilibrium reaction and corresponding expression for the thermodynamic solubility product constant K_{sp}° , derive an expression and calculate the value of the conditional equilibrium constant K_{sp}'



$$K_{sp}' = \frac{K_{sp}^{\circ}}{\gamma_{Pb^{2+}} \gamma_{I^{-}}^2} = \frac{7.9 \times 10^{-9}}{(0.36)(0.75)^2} \quad \mu = 0.10$$

$$= 3.9 \times 10^{-8}$$

- b) Calculate the molar solubility of the lead iodide.

$$PbI_2(s) \rightleftharpoons Pb^{2+} + 2I^{-}$$

$$K_{sp}' = [Pb^{2+}] [I^{-}]^2$$

$$[Pb^{2+}] = \frac{K_{sp}'}{[I^{-}]^2} \approx \frac{3.9 \times 10^{-8}}{(1.00 \times 10^{-3})^2}$$

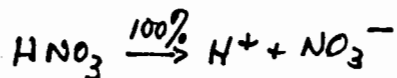
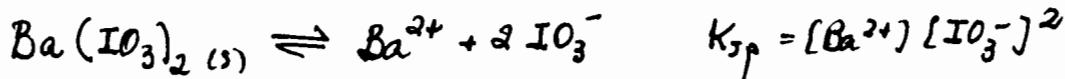
\uparrow +2x (cannot ignore)

$$= \underline{\underline{3.9 \times 10^{-2} \text{ M}}}$$

Use ~~quadratic~~ third order equation. No simple solution.

$$K_{sp}' = x(0.00100 + 2x)^2$$

4. (20) Consider a saturated solution of $\text{Ba}(\text{IO}_3)_2$ in aqueous 0.10 M nitric acid. Ignore activity coefficients.
- a) Write all of the equilibrium reactions, and corresponding equilibrium constant expressions, necessary to completely describe the equilibrium system. Be sure to include ionization of strong electrolytes.



- b) Write the charge balance equation for the aqueous solution.

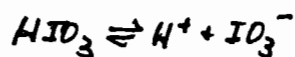
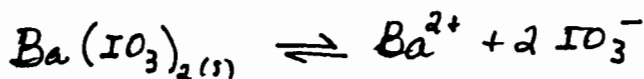
$$[\text{H}^+] + 2[\text{Ba}^{2+}] = [\text{OH}^-] + [\text{NO}_3^-] + [\text{IO}_3^-]$$

For c and d, assume that we maintain $[\text{H}^+] = 0.10$. Ignore activity coefficients.

- c) Calculate the fractional concentration of iodate (i.e., that fraction of total iodate in solution that is present as IO_3^-)

$$\alpha_{\text{IO}_3^-} = \frac{[\text{IO}_3^-]}{C_t} = \frac{1}{\frac{[\text{H}^+]}{K_a} + 1} = \frac{1}{\frac{0.10}{0.17} + 1} = 0.630 \approx 0.63$$

- d) Calculate the molar solubility of the $\text{Ba}(\text{IO}_3)_2$. Note that because $[\text{H}^+]$ is fixed, you will not need a charge balance equation.



$$C_{\text{IO}_3} = 2[\text{Ba}^{2+}]$$

$$K_{sp} = [\text{Ba}^{2+}] [\text{IO}_3^-]^2$$

$$[\text{IO}_3^-] = \alpha_{\text{IO}_3} C_{\text{IO}_3}$$

$$= [\text{Ba}^{2+}] (\alpha_{\text{IO}_3} C_{\text{IO}_3})^2$$

$$= [\text{Ba}^{2+}] (\alpha_{\text{IO}_3} 2[\text{Ba}^{2+}])^2$$

$$= 4 \alpha_{\text{IO}_3}^2 [\text{Ba}^{2+}]^3$$

$$[\text{Ba}^{2+}] = \left(\frac{K_{sp}}{4 \alpha_{\text{IO}_3}^2} \right)^{\frac{1}{3}} = \left(\frac{1.57 \times 10^{-9}}{4 (0.63)^2} \right)^{\frac{1}{3}} = (9.9 \times 10^{-10})^{\frac{1}{3}} \text{ mol/L}$$

$$= 1.0 \times 10^{-3} \text{ mol/L}$$

= solubility.