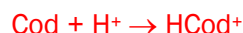


SHOW ALL WORK FOR CREDIT. STATE ANY ASSUMPTIONS MADE TO SOLVE A PROBLEM. STATE ALL ANSWERS WITH THE CORRECT NUMBER OF SIGNIFICANT FIGURES. ALL OF YOUR ANSWERS EXPRESSED IN SCIENTIFIC NOTATION MUST BE IN PROPER SCIENTIFIC NOTATION (i.e., 6.02×10^{23} not 6.02E23 or 6.02e23). EACH INSTANCE OF IMPROPER SCIENTIFIC NOTATION WILL RESULT IN THE LOSS OF THREE (3) POINTS. ALL NUMBERS THAT REQUIRE UNITS SHOULD HAVE THE UNITS WRITTEN. EACH INSTANCE OF A NUMBER WITHOUT THE REQUIRED UNITS WILL RESULT IN THE LOSS OF THREE (3) POINTS.

1. (30 points) A 0.552 g sample of codeine was dissolved in water to a total volume of 50.0 mL and titrated with 0.1103 M HCl. The equivalence point occurred at 16.71 mL. The pH of the solution at 10.0 mL of added acid was 8.00. From these data, determine the molar mass and K_b for codeine.



$$\text{mmol H}^+ = 16.71 \text{ mL} \times \frac{0.1103 \text{ mol H}^+}{\text{L}} = 1.843 \text{ mmol H}^+ = 1.843 \text{ mmol Cod @ equivalence point.}$$

$$\text{molar mass of Cod} = \frac{0.552 \text{ g Cod}}{1.843 \times 10^{-3} \text{ mol Cod}} = 299. \text{ g mol}^{-1}$$

When 10.0 mL of acid are added, we are partially neutralized so the solution is a buffer.

$$\text{mmol H}^+ = 10.0 \text{ mL} \times \frac{0.1103 \text{ mol H}^+}{\text{L}} = 1.103 \text{ mmol H}^+$$

$$\text{mmol Cod} = 1.843 \text{ mmol Cod}$$

$\text{Cod} + \text{H}^+ \rightarrow \text{HCod}^+$		
1.843	1.103	0.000
-1.103	-1.103	+1.103
0.740	0.000	1.103

$$\text{pH} = \text{pK}_a + \log \frac{[\text{B}]}{[\text{A}]}$$

$$\text{pK}_a = \text{pH} - \log \frac{[\text{B}]}{[\text{A}]} = 8.00 - \log \frac{0.740}{1.103} = 8.173$$

$$\text{pK}_b = \text{pK}_w - \text{pK}_a = 14.00 - 8.173 = 5.827$$

$$K_b = 10^{-\text{pK}_b} = 10^{-5.827} = 1.5 \times 10^{-6}$$

2. (10 points) Calculate the molar solubility of mercury(I) cyanide.



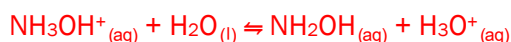
	Hg_2^{2+}	CN^-
I	0	0
C	+x	+2x
E	x	2x

$$K_{sp} = 5 \times 10^{-40} = [\text{Hg}_2^{2+}][\text{CN}^-]^2 = (x)(2x)^2 = 4x^3$$

$$x = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{5 \times 10^{-40}}{4}} = 5 \times 10^{-14}$$

The molar solubility is $5 \times 10^{-14} \text{ mol L}^{-1}$

3. (20 pts) What is the pH of a solution that is made by mixing 125.0314 g of hydroxylammonium nitrate with enough water to make 500.00 mL of solution?



$$K_a(\text{NH}_3\text{OH}^+) = \frac{K_w}{K_b(\text{NH}_2\text{OH})} = \frac{1.00 \times 10^{-14}}{1.1 \times 10^{-8}} = 9.1 \times 10^{-7}$$

$$[\text{NH}_3\text{OH}^+] = \frac{125.0314 \text{ g NH}_3\text{OHNO}_3}{500.00 \text{ mL} \times \frac{10^{-3} \text{ L}}{1 \text{ mL}}} \times \frac{1 \text{ mol NH}_3\text{OHNO}_3}{96.0428 \text{ g NH}_3\text{OHNO}_3} \times \frac{1 \text{ mol NH}_3\text{OH}^+}{1 \text{ mol NH}_3\text{OHNO}_3} = 2.6037 \text{ M}$$

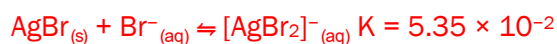
	NH_3OH^+	NH_2OH	H_3O^+
I	2.6037	0	10^{-7}
C	-x	+x	+x
E	$2.6037-x$	x	$10^{-7} + x$

$$K_a = 9.1 \times 10^{-7} = \frac{[\text{NH}_2\text{OH}][\text{H}_3\text{O}^+]}{[\text{NH}_3\text{OH}^+]} = \frac{(x)(10^{-7} + x)}{2.6037 - x} \approx \frac{x^2}{2.6037}$$

$$x = \sqrt{(2.6037)(9.1 \times 10^{-7})} = 1.538 \times 10^{-3} \approx [\text{H}_3\text{O}^+]$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(1.538 \times 10^{-3}) = 2.81$$

4. (25 pts) What is the concentration of silver ion in a solution that is 4.00 M sodium bromide and 1.50M silver nitrate. Keep in mind that silver can form both a precipitate with bromide and a complex ion.



Does a precipitate form?

$$[\text{Br}^-] = 4.00 \text{ M} - 2(1.50 \text{ M}) = 1.00 \text{ M}$$

$$Q = \frac{[\text{AgBr}_2]^-}{[\text{Br}^-]} = \frac{1.50}{1.00} = 1.50 > 5.35 \times 10^{-2}$$

So a precipitate does form. Set up ICE table.

	Br^-	$[\text{AgBr}_2]^-$
I	1.00	1.50
C	+x	-x
E	1.00+x	1.50-x

$$K = 5.35 \times 10^{-2} = \frac{[\text{AgBr}_2]^-}{[\text{Br}^-]} = \frac{(1.50 - x)}{(1.00 + x)}$$

$$5.35 \times 10^{-2} + 5.35 \times 10^{-2} x = 1.50 - x$$

$$1.0535x = 1.4465$$

$$x = 1.37$$

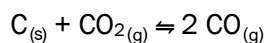
$$[\text{AgBr}_2]^- = 0.13 \text{ M}$$

$$[\text{Br}^-] = 2.37 \text{ M}$$

$$[\text{Ag}^+] = \frac{[\text{AgBr}_2]^-}{K_f [\text{Br}^-]^2} = \frac{0.13}{(1 \times 10^{11})(2.37)^2} = 2.3 \times 10^{-13} \text{ M}$$

$$[\text{Ag}^+] = \frac{K_{sp}}{[\text{Br}^-]} = \frac{5.35 \times 10^{-13}}{2.37} = 2.3 \times 10^{-13} \text{ M}$$

5. (25 pts) Consider the reaction:



$$K_c = 0.64 \text{ M at } 1200 \text{ K}$$

a. Calculate K_p for this reaction at 1200 K.

$$K_p = K_c (RT)^{\Delta n}$$

$$= (0.64 \text{ M}) \left((0.08314472 \text{ L bar mol}^{-1} \text{ K}^{-1}) (1200 \text{ K}) \right)^1 = 64 \text{ bar}$$

b. A reaction vessel at 1200 K initially contains 634 torr of CO . What is the equilibrium partial pressure of CO in this mixture? How many grams of carbon are produced if the volume of the container is 5.00 L?

$$634 \text{ torr} \times \frac{1.01325 \text{ bar}}{760 \text{ torr}} = 0.845 \text{ bar}$$

	CO_2	CO
I	0	0.845 bar
C	+x	-2x
E	X	8.45-2x

$$K_p = 64 \text{ bar} = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = \frac{(0.845 - 2x)^2}{x}$$

$$64x = 0.714 - 3.38x + 4x^2$$

$$4x^2 - 67.38x + 0.714 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}; a = 4; b = -67.38; c = 0.714$$

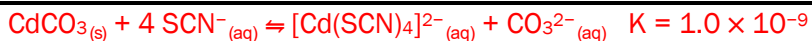
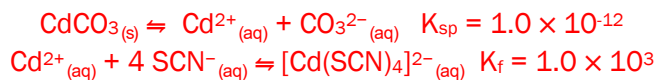
$$x = 0.0106037; \cancel{16.8344}$$

$$P_{\text{CO},eq} = 0.845 - 2x = 0.824 \text{ bar}$$

$$\frac{xV}{RT} = \text{moles of C produced} = \frac{(0.0106037 \text{ bar})(5.00 \text{ L})}{(0.08314472 \text{ L bar mol}^{-1} \text{ K}^{-1})(1200 \text{ K})} = 0.000531388 \text{ mol C}$$

$$0.000531388 \text{ mol C} \times \frac{12.011 \text{ g C}}{1 \text{ mol C}} = 0.00638 \text{ g C}$$

6. (25 pts) Calculate the molar solubility of cadmium carbonate in 1.00 M sodium thiocyanate solution.



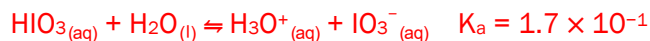
	SCN ⁻	[Cd(SCN) ₄] ²⁻	CO ₃ ²⁻
I	1.00	0	0
C	-4x	+x	+x
E	1.00-4x	x	x

$$K = \frac{[\text{Cd}(\text{SCN})_4]^{2-}[\text{CO}_3^{2-}]}{[\text{SCN}^{-}]^4} = \frac{(x)(x)}{(1.00-4x)^4} \approx \frac{x^2}{(1.00)^4} = x^2$$

$$x = \sqrt{K} = \sqrt{1.0 \times 10^{-9}} = 3.2 \times 10^{-5}$$

The molar solubility is 3.2×10^{-5}

7. (15 points) Calculate the pH of a 0.015 M solution of iodic acid.



	HIO ₃	H ₃ O ⁺	IO ₃ ⁻
I	0.015	10 ⁻⁷	0
C	-x	+x	+x
E	0.015 - x	10 ⁻⁷ + x	x

$$\frac{[\text{HIO}_3]}{K_{\text{a}}} = \frac{0.015}{0.17} = 0.088 < 100 \text{ so } "-x" \text{ should not be negligible in the denominator.}$$

$$K_{\text{a}} = \frac{[\text{IO}_3^{-}][\text{H}_3\text{O}^{+}]}{[\text{HIO}_3]} = \frac{(x)(10^{-7} + x)}{0.015 - x} \approx \frac{x^2}{0.015 - x}$$

$$x^2 + 0.17x - 0.00225 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} : a = 1; b = 0.17; c = -0.00225$$

$$x = \cancel{-0.183869}; 0.01386$$

$$x \approx [\text{H}_3\text{O}^{+}] = 0.01386$$

$$\text{pH} = -\log[\text{H}_3\text{O}^{+}] = -\log(0.01386) = 1.86$$