

Practice Final Exam

1. A chemist needs a buffer with pH 4.35. How many milliliters of pure acetic acid (density = 1.049 g/mL) must be added to 465 mL of 0.0941 M NaOH solution to obtain such a buffer?



Neutralization (limiting reactant) first. We know that the sodium hydroxide is the limiting reactant because we are left with a buffer. If the NaOH were in excess or in a stoichiometric ration with the acetic acid we would not have a buffer

$$n_{\text{OH}^-} = 465 \text{ mL} \times \frac{0.0941 \text{ mol}}{\text{L}} = 43.76 \text{ mmol}$$

	HPy	OH ⁻	Py ⁻
Initial moles	1	43.76	0
Loss of moles	-43.76	-43.76	+43.76
Final moles	1-43.76	0	43.76

$$\text{pH} = \text{p}K_a + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 4.74 + \log \frac{43.76}{1 - 43.76} = 4.35$$

$$\frac{43.76}{1 - 43.76} = 10^{-0.39} = 0.4073802$$

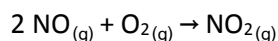
$$43.76 = (0.4073802)(1 - 43.76) = 0.4073802 - 17.82696$$

$$1 = \frac{43.76 + 17.82696}{0.4073802}$$

$$1 = 151.1780 \text{ mmol HC}_2\text{H}_3\text{O}_2$$

$$151.1780 \text{ mmol HC}_2\text{H}_3\text{O}_2 \times \frac{10^{-3} \text{ mol}}{1 \text{ mmol}} \times \frac{60.0520 \text{ g}}{\text{mol}} \times \frac{1 \text{ mL}}{1.049 \text{ g}} = 8.7 \text{ mL HC}_2\text{H}_3\text{O}_2$$

2. A study of the gas-phase oxidation of nitrogen monoxide at 25°C and 1.00 atm pressure gave the following results:



	<i>Conc. NO, mol/L</i>	<i>Conc. O₂, mol/L</i>	<i>Initial Rate</i>
Exp. 1	4.5×10^{-2}	2.2×10^{-2}	$0.80 \times 10^{-2} \text{ mol}/(\text{L}\cdot\text{s})$
Exp. 2	4.5×10^{-2}	4.5×10^{-2}	$1.60 \times 10^{-2} \text{ mol}/(\text{L}\cdot\text{s})$
Exp. 3	9.0×10^{-2}	9.0×10^{-2}	$1.28 \times 10^{-1} \text{ mol}/(\text{L}\cdot\text{s})$
Exp. 4	3.8×10^{-1}	4.6×10^{-3}	?

- a. What is the experimental rate law for the reaction above?

Between experiments 1 and 2 the concentration of O₂ is doubled and the rate is also doubled so the order with respect to O₂ is 1.

To find the order with respect to NO we need to do a little math...

$$\frac{R_3}{R_2} = \frac{1.28 \times 10^{-1} \text{ mol/L s}}{1.60 \times 10^{-2} \text{ mol/L s}} = 8.00 = \frac{k[\text{NO}]_3^n [\text{O}_2]_3^1}{k[\text{NO}]_2^n [\text{O}_2]_2^1} = \frac{(9.0 \times 10^{-2})^n (9.0 \times 10^{-2})^1}{(4.5 \times 10^{-2})^n (4.5 \times 10^{-2})^1} = 2^n \cdot 2$$

$$2^n = 4$$

$$n \log 2 = \log 4$$

$$n = \frac{\log 4}{\log 2} = \frac{0.6020599}{0.3010299} = 2$$

So the rate law is : $\text{Rate} = k[\text{NO}]^2 [\text{O}_2]$ where k is:

$$\text{Rate} = k[\text{NO}]^2 [\text{O}_2]$$

$$k = \frac{\text{Rate}}{[\text{NO}]^2 [\text{O}_2]} = \frac{0.80 \times 10^{-2} \text{ mol/L s}}{(4.5 \times 10^{-2} \text{ mol/L})^2 (2.2 \times 10^{-2} \text{ mol/L})} = 1.8 \times 10^2 \text{ L}^2 / \text{mol}^2 \text{ s}$$

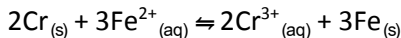
- b. What is the initial rate of the reaction in Experiment 4?

$$\text{Rate} = (1.8 \times 10^2 \text{ L}^2 / \text{mol}^2 \text{ s}) [\text{NO}]^2 [\text{O}_2]$$

$$= (1.8 \times 10^2 \text{ L}^2 / \text{mol}^2 \text{ s}) (3.8 \times 10^{-1} \text{ mol/L})^2 (4.6 \times 10^{-3} \text{ mol/L})$$

$$= 1.2 \times 10^{-2} \text{ mol/L s}$$

3. Consider the following cell reaction at 25°C.



Calculate the standard cell potential of this cell from the standard electrode potentials, and from this obtain ΔG° for the cell reaction. Use data below to calculate ΔH° . Use these values of ΔH° and ΔG° to obtain ΔS° for the cell reaction.

Substance	ΔH_f° (kJ mol ⁻¹)
Fe ²⁺ _(aq)	-89.1
Cr ³⁺ _(aq)	-143.5

The cathode is Fe²⁺ to Fe_(s) and the anode is Cr_(s) to Cr³⁺. The number of moles of electrons transferred is 6.

$$E^\circ(\text{Fe}^{2+}|\text{Fe}) = -0.447 \text{ V} \quad E^\circ(\text{Cr}^{3+}|\text{Cr}) = -0.744 \text{ V}$$

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = (-0.744 \text{ V}) - (-0.447 \text{ V}) = -0.297 \text{ V}$$

$$\Delta G^\circ = -nFE^\circ_{\text{cell}}$$

$$= -\left(\frac{6 \text{ mol e}^-}{\text{mol}}\right)\left(\frac{96485 \text{ C}}{\text{mol e}^-}\right)(-0.297 \text{ V}) = +1.719362 \times 10^5 \text{ J mol}^{-1}$$

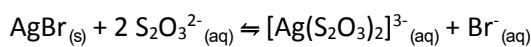
$$\Delta H^\circ = \left[\left(\frac{2 \text{ mol Cr}^{3+}}{\text{mol}}\right)\left(\frac{-143.5 \text{ kJ}}{\text{mol Cr}^{3+}}\right) + \left(\frac{3 \text{ mol Fe}}{\text{mol}}\right)\left(\frac{0.00 \text{ kJ}}{\text{mol Fe}}\right) \right] - \left[\left(\frac{2 \text{ mol Cr}}{\text{mol}}\right)\left(\frac{0.00 \text{ kJ}}{\text{mol Cr}}\right) + \left(\frac{3 \text{ mol Fe}^{2+}}{\text{mol}}\right)\left(\frac{-89.1 \text{ kJ}}{\text{mol Fe}^{2+}}\right) \right]$$

$$= -19.7 \text{ kJ mol}^{-1} = -1.97 \times 10^4 \text{ J mol}^{-1}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

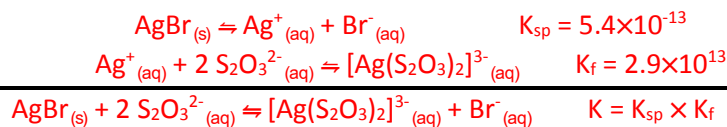
$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T} = \frac{-1.97 \times 10^4 \text{ J mol}^{-1} - 1.72 \times 10^5 \text{ J mol}^{-1}}{298.15 \text{ K}} = -577 \text{ J mol}^{-1} \text{ K}^{-1}$$

4. Crystals of AgBr can be removed from black-and-white photographic film by reacting the AgBr with sodium thiosulfate.



a. What is the equilibrium constant for this dissolving process?

The overall equation is a combination of the solubility of silver bromide and the complex ion formation of the dithiosulfatoargentate(I) ion.



$$K = K_{sp} \times K_f = (5.4 \times 10^{-13}) \times (2.9 \times 10^{13}) = 15.66$$

b. In order to dissolve 2.5 g of AgBr in 1.0 L of solution how many moles of Na₂S₂O₃ must be added?

Dissolving 2.5 g of AgBr in 1.0 L of solution tells us that the equilibrium concentration of the Br⁻ must be:

$$\frac{2.5 \text{ g AgBr}}{1.0 \text{ L}} \times \frac{1 \text{ mol AgBr}}{187.772 \text{ g AgBr}} \times \frac{1 \text{ mol Br}^{-}}{1 \text{ mol AgBr}} = 0.013314 \text{ M Br}^{-}$$

	S ₂ O ₃ ²⁻	Ag(S ₂ O ₃) ₂ ³⁻	Br ⁻
I	1	0	0
C	-2x	+x	+x
E	1-2x	x	x

$$K = \frac{[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}}{[\text{S}_2\text{O}_3^{2-}]^2} \frac{[\text{Br}^{-}]}{1} = \frac{(x)^2}{(1-2x)^2} = 15.66 = \frac{(0.013314)^2}{(1-2(0.013314))^2}$$

$$3.957271 = \frac{(0.013314)}{(1-2(0.013314))}$$

$$3.957271(1-0.026628) = 0.013314$$

$$1 = \frac{0.013314 + 0.026628}{3.957271} = 0.010 \text{ M S}_2\text{O}_3^{2-}$$

$$n_{\text{S}_2\text{O}_3^{2-}} = 1.0 \text{ L} \times \frac{0.10 \text{ mol S}_2\text{O}_3^{2-}}{\text{L}} = 0.10 \text{ mol S}_2\text{O}_3^{2-}$$

5. Tritium, or hydrogen-3, is formed in the upper atmosphere by cosmic rays, similar to the formation of carbon-14. Tritium has been used to determine the age of wines. A certain wine that has been aged in a bottle has a tritium content only 70% of that in a similar wine of the same mass that has just been bottled. How long has the aged wine been in the bottle? The half-life of tritium is 12.3 y.

$$\ln \frac{N_t}{N_0} = -kt \quad k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{12.3 \text{ y}} = 0.05635342 \text{ y}^{-1}$$

$$t = \frac{\ln \frac{N_t}{N_0}}{-k} = \frac{\ln(0.70)}{-(0.05635342 \text{ y}^{-1})} = 6.3 \text{ y}$$

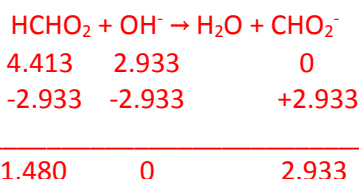
6. 25.00 mL of a 0.1765 M solution of formic acid is titrated with a 0.2144 M solution of potassium hydroxide.

(a) What is the pH of the solution when 13.68 mL of the sodium hydroxide solution have been added?

Neutralization first!

$$n_{OH^-} = 13.68 \text{ mL} \times \frac{0.2144 \text{ mol KOH}}{L} \times \frac{1 \text{ mol OH}^-}{1 \text{ mol KOH}} = 2.932992 \text{ mmol OH}^-$$

$$n_{HCHO_2} = 25.00 \text{ mL} \times \frac{0.1765 \text{ mol HCHO}_2}{L} = 4.41250 \text{ mmol HCHO}_2$$



We have some of the weak acid left over and have created its conjugate base so we have a buffer.

$$pH = pK_a + \log \frac{[B]}{[A]}$$

$$= 3.74 + \log \frac{2.933}{1.480} = 4.04$$

(b) What is the pH of the solution at the equivalence point?

At the equivalence point the moles of OH^- is equal to the moles of $HCHO_2$. The total volume can be found from:

$$4.41250 \text{ mmol OH}^- \times \frac{1 \text{ mol KOH}}{1 \text{ mol OH}^-} \times \frac{L}{0.2144 \text{ mol KOH}} = 20.58 \text{ mL KOH used}$$

$$\text{total volume} = 20.58 \text{ mL} + 25.00 \text{ mL} = 45.58 \text{ mL}$$

All of the moles of $HCHO_2$ are converted to the conjugate base, CHO_2^- . We can find the equivalence point pH by doing the weak base calculate with the conjugate base.

$$[CHO_2^-]_i = \frac{4.413 \text{ mmol } CHO_2^-}{45.58 \text{ mL}} = 0.09682 \text{ M}$$

$$K_b = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.6 \times 10^{-11}$$

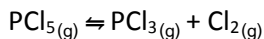
	CHO_2^-	OH^-	$HCHO_2$
I	0.09682	10^{-7}	0
C	-x	+x	+x
E	$0.09682 - x$	$10^{-7} + x$	x

$$K_b = \frac{[HCHO_2][OH^-]}{[CHO_2^-]} = \frac{(x)(10^{-7} + x)}{(0.09682 - x)} \approx \frac{(x)(x)}{(0.09682)} = 5.6 \times 10^{-11}$$

$$x = \sqrt{(5.6 \times 10^{-11})(0.09682)} = 2.319 \times 10^{-6} \approx [OH^-] \quad \text{approximation is valid here (4.3\%)}$$

$$pOH = -\log[OH^-] = 5.6347 \quad pH = 14.00 - pOH = 8.37$$

7. Phosphorus(V) chloride, PCl_5 , dissociates on heating to give phosphorus(III) chloride, PCl_3 , and chlorine.



A closed 2.00-L vessel initially contains 0.0100 mol PCl_5 . What is the total pressure at 250°C when equilibrium is achieved? The value of K_c at 250°C is 4.15×10^{-2} .

First find K_p because we want the pressure of the system.

$$K_p = K_c (RT)^{\Delta n} = (4.15 \times 10^{-2}) \left((0.083144 \text{ L bar mol}^{-1} \text{ K}^{-1})(523 \text{ K}) \right)^{(2-1)} = 1.804598$$

Initial pressure of PCl_5 :

$$P_{\text{PCl}_5} = \frac{nRT}{V} = \frac{(0.0100 \text{ mol PCl}_5)(0.083144 \text{ L bar mol}^{-1} \text{ K}^{-1})(523 \text{ K})}{(2.00 \text{ L})} = 0.2174 \text{ bar}$$

Set up ICE table:

	PCl_5	PCl_3	Cl_2
I	0.2174	0	0
C	-x	+x	+x
E	0.2174-x	x	x

Calculate:

$$K_p = \frac{P_{\text{PCl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{x^2}{(0.2174 - x)} = 1.80$$

$$x^2 + 1.80x - 0.391 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(1.80) \pm \sqrt{(1.80)^2 - 4(1)(-0.391)}}{2(1)} = \cancel{-1.9959} \text{ or } 0.19590$$

$$P_T = P_{\text{PCl}_5} + P_{\text{PCl}_3} + P_{\text{Cl}_2} = (0.2174 - x) + x + x = 0.2174 + x = 0.431 \text{ bar}$$

8. Answer the following questions about transition metal chemistry.

a. $[\text{Fe}(\text{HOC}_6\text{H}_4\text{COO})_3]$ is purple. The salicylate ion, $\text{HOC}_6\text{H}_4\text{COO}^-$, is a bidentate ligand. What hybridization is the iron ion using in the complex ion? Explain your reasoning.

The oxidation state of the iron is 3+ so it has 5 electrons in the d orbitals. Because the ligand is bidentate the coordination number is 6 so the geometry is octahedral. Therefore the hybridization is either d^2sp^3 or sp^3d^2 . The color of complex is purple so it absorbs orange which means that the Δ is small which means that the electrons pair up before moving to higher d levels which means that the two higher d orbitals are open so the hybridization is d^2sp^3 .

b. $\text{Cd}(\text{H}_2\text{O})_6^{2+}$ is colorless. Explain why this would be expected.

The Cd^{2+} ion has 10 electrons in the d orbitals so there can be no transitions of electrons between d levels to give rise to a color.

c. The fluoride ion is a weakly bonding ligand. What color would you expect to see in the FeF_6^{4-} ion? Explain.

Because the ligand is weakly bonding the Δ should be small so the color absorbed should be in the red/yellow/orange part of the spectrum so we would see the green/blue/purple color.

d. Name $\text{K}_2[\text{Cr}(\text{CO}_3)_2(\text{en})_2]$. What is the coordination number of the chromium ion?

Potassium dicarbonatobis(ethylenediamine)chromate(IV). The coordination number is 6 because the carbonate is monodentate (2x1) and the ethylenediamine is bidentate (2x2).