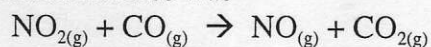


1. For each of the following situations, please answer the question in one or a few words, or indicate that there is INSUFFICIENT INFORMATION for you to be sure of the answer. Although you need not do so for full credit, if you would like to ensure that I understand the reasoning behind your answer, you may justify your choice in one short sentence. (2 points each)

a) One of the reactions that we discussed in class was



This reaction is second order with respect to NO_2 . If two experiments are performed in which the $[\text{CO}]$ is kept constant, but the $[\text{NO}_2]$ is three times as high in experiment #2 as in experiment #1, how much faster would you expect the rate of reaction to be in experiment #2?

Nine times as fast (3^2)

b) Consider the decomposition of dinitrogen pentoxide gas:



An experiment is performed in which it is found that nitrogen dioxide is formed at a rate of 3.6 M/sec. What would you predict to be the rate of formation of molecular oxygen in this experiment?

0.9 M/sec ($3.6 \div 2 \times 0.5$)

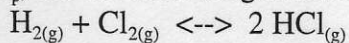
c) True or false: Mole for mole, sugar is less effective as a sidewalk de-icer than is salt because the sugar forms strong hydrogen bonds with the water molecules while the salt does not.

False. It is less effective, but NOT for this reason.

d) In the desert southwest, some people employ a kind of air-conditioner known as a swamp cooler. In this device, hot air is blown through a mist of water droplets. If the air *comes out cooler than it went in*, would you expect that the air: (A) causes the gaseous water vapor to condense into droplets, OR (B) causes the water droplets to vaporize into gas?

B. Air comes in warm, causes vaporization and thus loses energy to the water, so it comes out cooler.

e) At 25°C, the equilibrium constant (K_p) for the following reaction is 2.5×10^{33} .



At this temperature, does this reaction favor the formation of hydrogen chloride or its decomposition?

This K_p value is HUGE. FORMATION of $\text{HCl}_{(g)}$ is strongly favored.

f) Consider two reactions occurring at a certain temperature. In reaction A, the products of the reaction are more stable than the reactants; in reaction B, the reactants are more stable. Which reaction will be faster?

INSUFFICIENT INFO available - relative energies tell us only about K_{eq} , not rates.

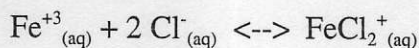
g) Consider two reactions occurring at a certain temperature. For reaction A, the activation energy is 85 kJ/mol; for reaction B, it is 65 kJ/mol. Which reaction will be faster?

B. Lower E_{act} = faster.

h) Consider a solution of a salt in water. Some of the pertinent details are: molar mass of the salt = 100 g/mol; 10.0 grams of the salt were dissolved in 100.0 mL of water at 4°C; the volume of the resulting solution was 101.2 mL, the density of water at 4°C is 1.00000 g/mL; the density of the solution was 1.087 g/mL; the concentration of water molecules in pure water is 55.5 M. What is the concentration of the salt in the solution in *units of mass percent*?

$$\text{mass percent} = \frac{\text{grams salt}}{\text{grams total}} = \frac{10}{10+100} = \frac{10}{110} = 0.0909 = \boxed{9.09\%}$$

i) Please write the equilibrium constant expression (K_c or K_{eq}) for the following reaction that you observed in lab two weeks ago:

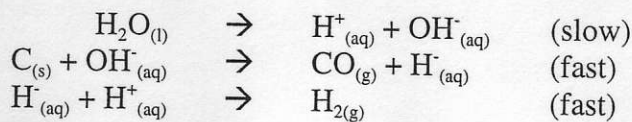


$$K_{eq} = \frac{[\text{FeCl}_2^{+}]}{[\text{Fe}^{3+}][\text{Cl}^{-}]^2}$$

j) True or false: Increasing the temperature of a reaction AND increasing the concentration of one of the reactants BOTH increase the rate constant for the reaction.

False. Changing concentration may change the rate, but it has no effect on the rate constant.

2. At high temperature and pressure, water passed over coke (carbon obtained from coal, not the cola or the psychoactive substance) reacts to form carbon monoxide and elemental hydrogen. The following mechanism is proposed for the reaction:



Suppose that you want to design some experiments to test the proposed mechanism.

a) Under the proposed mechanism, what would be the rate law for the reaction? (8 points)

rate = $k[\text{H}_2\text{O}]$ - this reflects the molecularity of the rate-determining step.

2 pts. form
pts molecularity
of overall
- 4 pts for
wrong side of
RDS

b) According to this mechanism, what effect would you expect to see on the initial rate if the starting concentration of coke were tripled? Please *rigorously* justify your answer. (4 points)

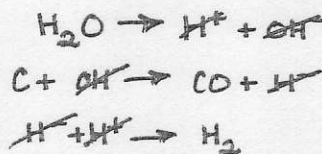
The rate, according to this mechanism, is independent of $[\text{C}]$.
Therefore there should be no effect on rate.

should have
switched
points!

1 pt for
rough logz
2 pt for vague
but correct
1 pt for right
answer, wrong reason

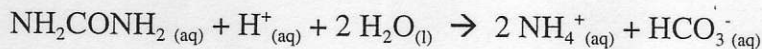
c) Under the proposed mechanism, what would be the balanced chemical equation for the overall reaction? (8 points)

add up the elementary reactions:



- 2 states
- 6 RDS only

3. Urea (NH_2CONH_2) is the end product of protein degradation in our bodies. Urea can be further broken down in acidic solutions as follows:



This reaction is first order with respect to urea, and first order overall.

a) Please write the rate law for this reaction. (3 points)

$$\text{rate} = k [\text{urea}]$$

b) Urea is degraded at a rate of $4.00 \times 10^{-6} \text{ M/sec}$ when its concentration is 0.150 M at 21°C . What is the rate constant for this reaction (at this temperature)? (Please remember to report your answer to the proper number of significant figures and with the appropriate units.) (7 points)

$$\text{rate} = 4.00 \times 10^{-6} \text{ M/sec} = k [\text{urea}] = k (0.150)$$

$$k = \frac{4.00 \times 10^{-6}}{0.150} = 2.67 \times 10^{-5} \text{ sec}^{-1}$$

4 method
1 answer
1 SE
1 units

c) If a 25.0 mM solution of urea were allowed to break down at 21°C as in part (b), how long would it take until the concentration was decreased 1000 fold (to $25.0 \mu\text{M}$)? (10 points)

$$\ln [\text{urea}]_t = -kt + \ln [\text{urea}]_0$$

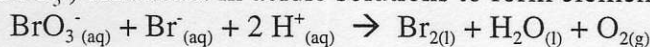
$$\ln (25 \times 10^{-6}) = (-2.67 \times 10^{-5})t + \ln (25 \times 10^{-3})$$

$$-10.5966 + 3.6888 = -2.67 \times 10^{-5} t$$

$$t = 258,716 \text{ sec} \Rightarrow 259,000 \text{ sec}$$

-9 if use
rate law
-3 if use
wrong order

4. Bromide and bromate (BrO_3^-) ions react in acidic solutions to form elemental bromine:



A curious experimentalist decides to perform some experiments to better understand this reaction. Her data are shown below (all experiments performed at 25°C):

Expt #	$[\text{BrO}_3^-]_0$, M	$[\text{Br}^-]_0$, M	$[\text{H}^+]_0$, M	initial rate of formation of Br_2 , M/sec
1	0.100	0.100	1.00×10^{-3}	2.31×10^{-7}
2	0.200	0.100	2.00×10^{-3}	1.85×10^{-6}
3	0.200	0.100	1.00×10^{-3}	4.50×10^{-7}
4	0.200	0.050	2.00×10^{-3}	9.16×10^{-7}

a) Please write the rate law for this reaction. (13 points)

2 pts. basic format

3 Comparing experiments 1 & 3, $[\text{BrO}_3^-]$ increases by a factor of 2, rate roughly doubles.

3 2 & 3, $[\text{H}^+]$ decreases 2x, rate decreases ~4x

3 2 & 4, $[\text{Br}^-]$ decreases 2x, rate decreases ~2x

Therefore,

$$\text{rate} = k [\text{BrO}_3^-] [\text{Br}^-] [\text{H}^+]^2$$

2

-4 if one missing

b) What is the rate constant for this reaction at this temperature? (Please remember to report your answer to the proper number of significant figures and with the appropriate units.) (7 points)

$$\text{rate} = k [\text{BrO}_3^-] [\text{Br}^-] [\text{H}^+]^2$$

Ideally, one should calculate k for each experiment and average them. Given that time is limited here, ~~we~~ solve for k in any one reaction.

For example:

$$\begin{aligned} 2.31 \times 10^{-7} &= k (0.1) (0.1) (1 \times 10^{-3})^2 \\ &= k (1.0 \times 10^{-8}) \end{aligned}$$

$$k = 23.1$$

$$\frac{\text{M}}{\text{sec}} = k \cdot \text{M} \cdot \text{M} \cdot \text{M}^2 = k \cdot \text{M}^4$$

$$k \therefore = \text{M}^{-3} \text{sec}^{-1}$$

$$k = 23.1 \text{ M}^{-3} \text{sec}^{-1}$$

3 plug

1 solve

1 answer

1 SF

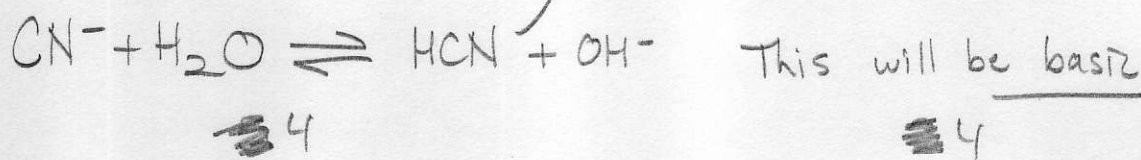
1 units

That's the net ionic equation

8. **Acid/base equilibria.** Cyanide is a potent metabolic toxin. Compounds containing the cyanide ion often have a characteristic "bitter almond" smell; this smell is also released by scratching the bark of cherry trees, a good diagnostic test for the genus *Prunus*. A few years ago, there was considerable agitation in the Kentucky horse-breeding community when foals started dying without an apparent cause. It was eventually determined that the victims had eaten grass that contained a large number of caterpillars. And the caterpillars had high levels of cyanide in their systems as a result of growing up on a diet of cherry tree leaves.

The protonated form of the cyanide ion is cyanic acid, which has a K_a of 3.3×10^{-4} .

a) (8 points) Suppose that in the course of the investigation into the foals' death, an enterprising chemist had purified some of the cyanide (in the form of sodium cyanide, NaCN, 49.0 g/mol) from a sample of caterpillar tissue. If 5.00 grams of the sodium cyanide sample were dissolved in water to a final volume of 100.0 mL, would you expect the resulting solution to be **acidic, basic, or neutral**? Please write a **balanced chemical equation** supporting your prediction.



(Net ionic)

b) (15 points) What should be the pH of the solution in part (a)? Give eq?

$\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$	2
I 1.02 M	0
C	0
E 1.02 - x	x
	3

$$\frac{x^2}{1.02 - x} = K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{3.3 \times 10^{-4}} = 3.03 \times 10^{-11}$$

$$x = 5.56 \times 10^{-6} \text{ (assump r)}$$

$$= [\text{OH}^-]$$

$\text{pH} = 8.75$

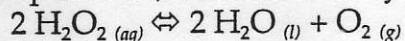
$$[\text{CN}^-] = \frac{5 \text{ g NaCN}}{0.1 \text{ L}} \times \frac{1 \text{ mol}}{49 \text{ g}} = 1.02 \text{ M}$$

c) (7 points) Silver ions form an insoluble salt with cyanide ions (AgCN , $K_{sp} = 1 \times 10^{-12}$). If silver nitrate were added to the solution in (b), would you expect the pH to go up, go down, or stay the same? Please justify your answer using either quantitative or qualitative logic. **PROVIDE THEM AN EQN or use diff eq.**

Ag^+ will decrease $[\text{CN}^-]$, pulling rxn LEFT. Thus $[\text{OH}^-]$ goes down,

pH goes down

i. (15 points) The liver is an important site of detoxification in mammals. One of the enzymes found in the liver that plays an important role in removing toxic or otherwise dangerous compounds from the blood is catalase. This enzyme accelerates the breakdown of peroxides, which can be very damaging, as they oxidize important cellular components. The following reaction shows the decomposition of hydrogen peroxide, a reaction catalyzed by catalase:



In a closed vessel containing an equilibrium mixture of hydrogen peroxide, water, and oxygen,

a) Will an increase in pressure cause the reaction to shift to the right, to the left, or not to shift at all?

2 TO LEFT (to reduce mols gas)

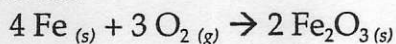
b) the decomposition of hydrogen peroxide is quite exothermic. Will cooling the container cause the equilibrium to shift to the right, to the left, or not at all?

2 TO RIGHT (to "replenish" heat)

c) Would you expect the equilibrium constant for this reaction to be equal to one, less than one, or greater than one? Please explain your reasoning.

3
(~~1+2~~) GREATER THAN ONE (Exothermic)

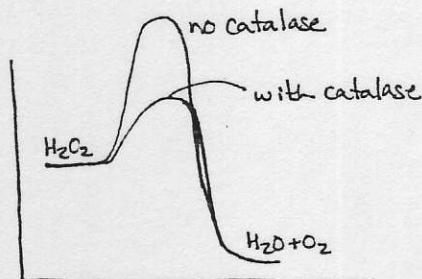
d) If solid iron were introduced into the vessel, and formed rust according to the equation below, would you expect the hydrogen peroxide equilibrium to shift to the right, to the left, or not at all?



2 TO RIGHT (to replenish O_2)

e) Please sketch out an energy profile diagram for the decomposition of hydrogen peroxide as written above, both in the presence and absence of the enzyme catalase.

2+2

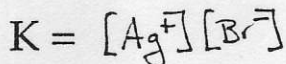


f) If catalase were introduced into the vessel, would you expect the equilibrium to shift to the right, to the left, or not at all?

2 NOT AT ALL (catalyst affects E_a + rate, NOT ΔE + K_{eq})

4. (22 points) Silver bromide (AgBr) is a sparingly soluble salt used in photographic emulsions to produce an image upon exposure to light.

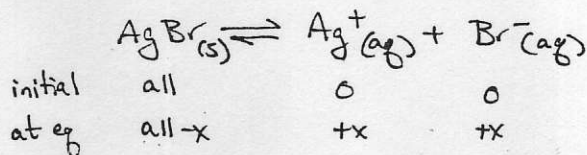
a) Please write an expression for the equilibrium constant for solid silver bromide dissolving in water.



-1 pt for no charges
2 pts if include
AgBr(s) & H₂O(l)

1 pt. for something

b) If the value for this equilibrium constant is 4×10^{-13} , what is the molar solubility of silver bromide?



$$K_{sp} = 4 \times 10^{-13} = x^2 \quad x = [Ag^+] = [Br^-]$$

= molar solubility

$$\boxed{6 \times 10^{-7} M}$$

-1 for units
-1 for real and sig fig

c) To increase the molar solubility of silver bromide, you could add one of the following to the solution: Ag⁺, Br⁻, H⁺, NH₃. Based on what you know of chemical equilibria and what you have done in lab, which would you choose to add, and why?

Only NH₃ will shift the solubility equilibrium to the right, that is, FAVORING SOLUBILITY.

This happens when NH₃ forms a complex ion w/ silver, as in your qualitative analysis lab. (H⁺ will have an insignificant effect as HBr is a

d) Will adding the substance you chose in part (c) cause the value of K_{sp} to increase, decrease, or stay the same? **STRONG ACID and dissociates ≈ 100%**

K_{sp} will be unchanged; only the position of the equilibrium will shift.

1. **Fundamental concepts, terminology, and observations.** Please answer the following questions briefly unless asked for a more detailed explanation. (3 points each)

- a) Consider two reactions. Reaction A is slow, but at equilibrium, the reaction products are more stable than the reactants. Reaction B is faster but less thermodynamically favorable than A. If a catalyst is introduced into reaction vessel A so that reaction A now occurs at the same rate as B, **will the equilibrium constant for A be bigger than that for B, smaller than B, or equal to B** (or can't you be sure from this information)?

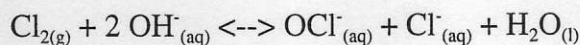
In reaction A (whether the catalyst is there or not), products are more stable and thus will predominate at equilibrium.

K_{eq} is bigger for A.

- b) Arsenic acid has a K_a of 6.0×10^{-3} ; benzoic acid has a K_a of 6.6×10^{-5} . **Which is the stronger acid?**

Arsenic acid

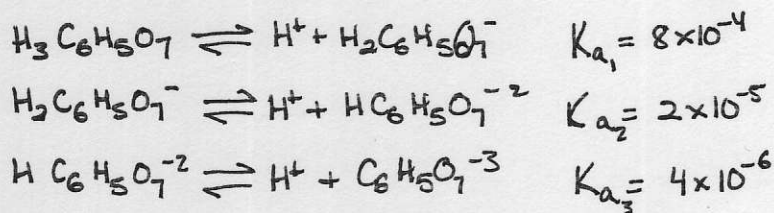
- c) Household bleach consists of an aqueous solution of 5% sodium hypochlorite, NaOCl. It is produced from (poisonous) chlorine gas according to the following reaction:



Containers of bleach often bear the warning that it should not be mixed with acidic solutions (such as tile cleaner). Please **briefly** explain why mixing bleach and acid might generate toxic fumes.

Adding acid should shift equilibrium to the left by reacting with the hydroxide ions, thus reducing their concentration. This shift will lead to the production of toxic chlorine gas.

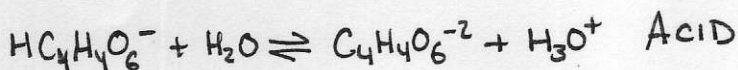
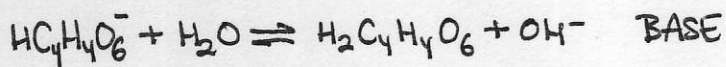
- d) Citric acid ($\text{H}_3\text{C}_6\text{H}_5\text{O}_7$) is responsible for the sour taste of many commercial beverages and candies. It is a triprotic acid with K_a values of 8×10^{-4} , 2×10^{-5} , and 4×10^{-6} . What is the value of the base dissociation constant (K_b) for disodium monohydrogen citrate?



$$K_b \text{ for } \text{Na}_2\text{HC}_6\text{H}_5\text{O}_7 = \frac{K_w}{K_{a_2}} = \frac{10^{-14}}{2 \times 10^{-5}} = 5 \times 10^{-10}$$

1/26
1/20/03

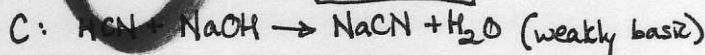
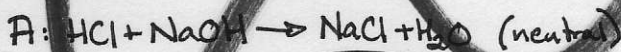
- e) Potassium hydrogen tartrate, $\text{KHC}_4\text{H}_4\text{O}_6$, is an amphoteric salt produced in winemaking and known by cooks as cream of tartar. Please write **one balanced chemical equation showing the acidic behavior of this salt in water**, and **one equation showing its basic behavior**. Be sure to label which equation is which.



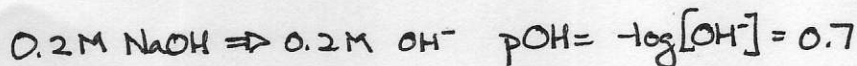
- f) Hydroiodic acid is a strong acid while its cousin hydrofluoric acid is weak, with a K_a of 6×10^{-4} . Please tell me whether the dissociation of **each** of these acids will be accompanied by a **positive or negative change in energy (ΔE)** (or whether you can't tell from this information).



- g) Consider three beakers: into beaker A are poured 50 mL of 0.1 M HCl and 50 mL of 0.1 M NaOH, into beaker B are poured 50 mL of 0.1 M HCN and 50 mL of 0.1 M NaCN, and into beaker C are poured 50 mL of 0.1 M HCN and 50 mL of 0.1 M NaOH. Please indicate the letter of every beaker that contains a buffer solution.

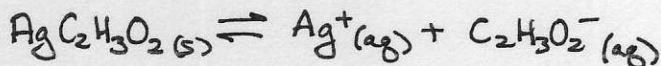


- h) One of the solutions that you had available to you yesterday in lab was labeled "0.2 M NaOH". What do you **predict the pH** of this solution to be (or can't you tell from this information)?



$$\text{pH} = 14 - \text{pOH} = \boxed{13.3}$$

- i) Two weeks ago in lab, you determined the solubility of silver acetate in water. Would you expect this sparingly soluble salt to be **more soluble in water or in a solution buffered at a pH of 3**?



At pH 3, H^+ ions will bind $\text{C}_2\text{H}_3\text{O}_2^-$ ions and shift the eq. to the right,

- j) For a bit more challenge... Consider two monoprotic acids titrated with the same solution of potassium hydroxide. If the titration of acid #2 reaches a higher pH at the endpoint than does the titration of acid #1, **which acid is stronger** (or can't you tell from this information)?

Acid #2 has higher pH at equivalence point. Thus conj. base #2 is a stronger base, so acid #2 is a weaker acid. Acid #1 is stronger.

2. Places we've been: predicting the relative acidity of substances

a) Please indicate which member of the following pairs of compounds you predict to be more strongly acidic, **and** indicate which features of the molecular structure lead to your decision and why these features are important. (If you have any questions about the structures of these molecules, please ask!) (6 points)

HClO and HF

HF stronger: H-F bond more polarized than H-OCl bond. This permits more facile ionization.

or 1 pt answer
1 pt feature
1 pt why
1/2 value
if logic right,
choice wrong

H₂SO₄ and H₃PO₄

H₂SO₄ stronger: HSO₄⁻ anion more stable than H₂PO₄⁻ anion due to increased Electronegativity of S vs. P. This favors dissociation/ionization relative to H₃PO₄.

b) Suppose that the following salts are dissolved in water. Please **pick two out of the three** and indicate whether you expect each solution to be acidic, basic, or neutral. *Briefly* justify your choices. (4 points)

NaBrO

Basic. BrO⁻ is the conj. base of HBrO, a weak acid.

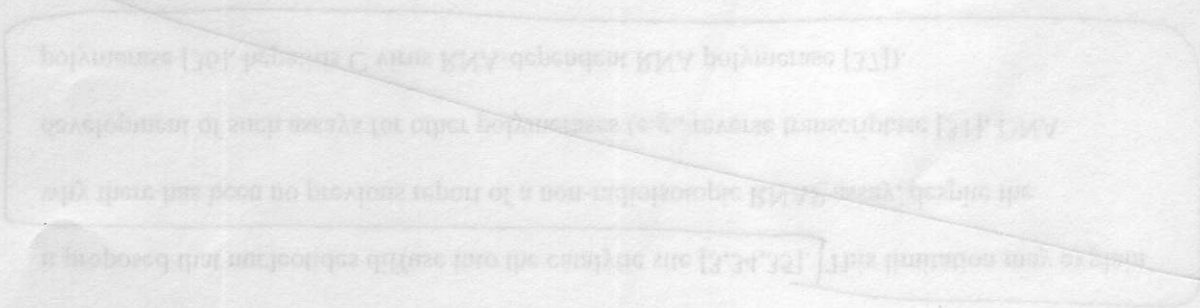
Cu(NO₃)₂

Neutral. NO₃⁻ is the conj. base of HNO₃, a strong acid.

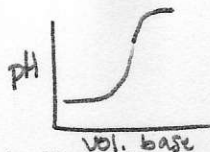
NH₄Br

Acidic. NH₄⁺ is the conj. acid of NH₃, a weak base.

Remember that you
are responsible for the
calculations & questions
pertaining to the titration simulation
exercises from week #11.



F111



3. In lab yesterday, you had the opportunity to construct and test buffers with several different chemistries, including an acetic acid/sodium acetate buffer. As you know from lab a week ago, acetic acid has a K_a of 1.8×10^{-5} at 25°C .

a) Suppose that a sample of acetic acid were prepared by dissolving 0.13 moles of acetic acid in 520 mL of water. If that solution was then titrated to the equivalence point with 0.1000 M NaOH as you did in lab last week, what should be the **total volume of the solution** at the equivalence point? (4 points)

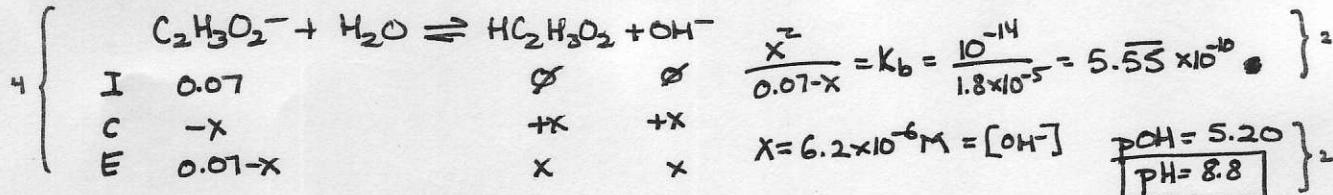
$$0.13 \text{ moles acid} \times \frac{1 \text{ mole base}}{1 \text{ mole acid}} \times \frac{1 \text{ L NaOH soln}}{0.1000 \text{ mol NaOH}} = 1.3 \text{ L}$$

+ 520 mL starting vol = 1.82 L

b) Following on part (a), what would you predict to be the pH of the solution at the equivalence point? (If you are unsure of your answer to part (a), you may assume that the volume at the equivalence point is 1.82 L) (12 points)

2 { At equivalence, the solution contains Na^+ , H_2O , and $\text{C}_2\text{H}_3\text{O}_2^-$.
↳ this is weakly basic.

2 { $\frac{0.13 \text{ mol } \text{C}_2\text{H}_3\text{O}_2^-}{1.82 \text{ L}} = 0.07 \text{ M } \text{C}_2\text{H}_3\text{O}_2^-$



c) If a new solution was made by combining 180 mL of 1.0 M acetic acid with 120 mL of 1.0 M sodium acetate, what would you predict to be the resulting pH? (4 points)

You can solve this w/ an ICE box, but the Henderson-Hasselbalch eqn. is easier:

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

$$= 4.74 + \log \left[\frac{(0.4)}{(0.6)} \right] = \boxed{4.56}$$

4. In one part of the qualitative analysis that you performed in lab several weeks ago, you created the insoluble salt iron (III) hydroxide.

a) If the pH of a saturated solution of iron (III) hydroxide is 11.68, what is the **hydroxide ion concentration** in this solution? (3 points)

pH = 11.68

pOH = 14 - pH = 2.32 $[OH^-] = 10^{-pOH} = 4.79 \times 10^{-3} M$

-2 if key relationship wrong

b) Given this hydroxide ion concentration at equilibrium, please **calculate the solubility product constant (K_{sp})** for iron (III) hydroxide at this temperature. (If you are unsure of your answer to part (a), you may assume a hydroxide ion concentration of $4.8 \times 10^{-3} M$.) (7 points)

	$Fe(OH)_3(s) \rightleftharpoons Fe^{+3} + 3OH^-$	$K_{sp} = [Fe^{+3}][OH^-]^3$	} 2+1 pts.
I	0	0	} 2 pt.
C	+x	+3x	
E	x	3x	

from above, $3x = 4.79 \times 10^{-3}$
 $x = 1.60 \times 10^{-3}$

$27x^4 = K_{sp} = 1.75 \times 10^{-10}$

} 2 pts.

c) In a subsequent step in the analysis you performed in lab, you dissolved the iron hydroxide precipitate by adding a few drops of nitric acid. Please explain thoroughly why the addition of nitric acid should increase the solubility of this salt. (5 points)

A strong acid is a source of H^+ ions. These will react w/ OH^- to produce H_2O , thus reducing the hydroxide ion concentration. By LeChatelier's principle, this will drive the equilibrium to the right, increasing solubility.

d) Logic suggests that if solubility of iron (III) hydroxide is *increased* in an acidic solution, it should be *decreased* in a basic one. Please test this suggestion by **calculating the molar solubility** of iron (III) hydroxide in a solution buffered at pH 13.0. (5 points)

	$Fe(OH)_3(s) \rightleftharpoons Fe^{+3} + 3OH^-$	pH = 13.0 pOH = 1.0 $OH^- = 0.1 M$	} 1/2 pts.
I	0	0.1	} 2 pts.
C	+x	+3x	
E	x	(0.1+3x)	

$K_{sp} = 1.75 \times 10^{-10} = (x)(0.1+3x)^3$

assuming $3x \ll 0.1$,
 $x \approx 1.75 \times 10^{-7}$. Assumption is legit.

} 2 pts.

In water, solubility was $1.6 \times 10^{-3} M$
 At pH 13, solubility is $1.7 \times 10^{-7} M$. Way down.

1. For each of the following situations, please answer the question in one or a few words, or indicate that there is INSUFFICIENT INFORMATION for you to be sure of the answer. Although you need not do so for full credit, if you would like to ensure that I understand the reasoning behind your answer, you may justify your choice in one short sentence. (2 points each)

a) If the reaction quotient, Q , is less than the equilibrium constant for a particular chemical system, then what must change for the system to reach equilibrium?

If $Q < K_{eq}$, [products] too small, reaction must go towards products

b) Consider an acetic acid/sodium acetate buffer at pH 5.0. Given what you have experimented with in lab, what do you expect to happen to the pH of the buffer if silver nitrate is added to the solution (assuming no change in volume) -- will the pH go up, down, or not change?

Silver nitrate \rightarrow AgAc will ppt. Thus $[OAc^-]$ will decrease. Thus more OAc will dissociate. Thus pH will decrease.

c) Iron (II) hydroxide has a K_{sp} of 7.9×10^{-16} , and copper (II) hydroxide has a K_{sp} of 4.8×10^{-20} at $25^\circ C$. Will addition of Cu^{+2} ions to a solution of iron (II) hydroxide cause the $Fe(OH)_2$ solubility to increase or decrease, or will it have no effect? (Assume that the volume does not change.)

Cu^{+2} will precipitate $Cu(OH)_2$. Thus the reaction move to the right, and solubility will increase

d) Citric acid ($H_3C_6H_5O_7$) is a weak triprotic acid with three K_a values: 4.0×10^{-7} , 1.7×10^{-5} , and 7.4×10^{-4} . Which is the stronger acid, dihydrogen citrate or monohydrogen citrate?

Dihydrogen citrate.

e) Flasks A and B contain 0.01 mole samples of different but unknown acids. They are titrated with the same NaOH solution. If both flasks require 25.1 mL of titrant to reach the equivalence point, is it safe to say that both unknown acids must have the same K_a ?

No! Same volume \Rightarrow same moles acid. \neq same K_a !

- f) Suppose that I dissolve 0.5 moles of sodium nitrate in water in one beaker to a final volume of 400 mL and 0.5 moles of sodium nitrite in a second beaker to the same final volume. I then offer you \$10 if you can pick the beaker with a basic pH. Will you pick the nitrate beaker, the nitrite beaker, both beakers, or is there no way to win your \$10?

Nitrite (conjugate base of a weak acid)

- g) I want to create a buffer at pH = 6.5. I have access *only* to NaOH and the following substances: hydrochloric acid, arsenous acid ($K_a = 5.1 \times 10^{-1}$), formic acid ($K_a = 1.8 \times 10^{-4}$), carbonic acid ($K_a = 4.3 \times 10^{-7}$), and ammonia ($K_b = 1.8 \times 10^{-5}$). If these are my only choices, which should I choose as the basis for my buffer, or will they all work equally well?

HCl - strong acid X

Arsenous - pK_a much too low X

Formic - $pK_a = 3.7$. not good X

Carbonic $pK_a = 6.4$ almost = pH target. good.

Ammonia - weak base. X

- h) 0.05 moles of NaOH and 0.04 moles of HCl are mixed in a solution whose final volume is 100 mL. What is the final pH of this solution?

0.05 mol OH^-

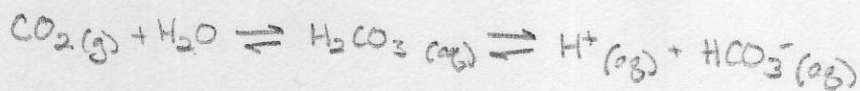
0.04 mol H^+

0.01 mol OH^- left after reaction. $pOH = -\log\left(\frac{0.01}{0.1}\right) = 1$ pH = 13

- i) HX is a strong acid; HY is a weak acid. Will the *rate constant* for the dissociation of HX be larger than, smaller than, or equal to the rate constant for the dissociation of HY?

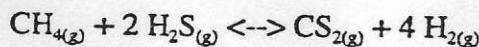
Insufficient info.

- j) Consider a bottle of carbonated water. Will the pH of the solution increase, decrease, or stay the same when the bottle is opened?



Opening bottle reduces P_{CO_2} , reduces $[CO_2]$. Thus $[H_2CO_3] \downarrow$, $[H^+] \downarrow$, pH \uparrow

3. Methane gas reacts with hydrogen sulfide to form elemental hydrogen according to the following reaction:



$$K_{eq} = \frac{[\text{H}_2]^4 [\text{CS}_2]}{[\text{H}_2\text{S}]^2 [\text{CH}_4]}$$

a) 3.0 moles of methane, 2.2 moles of hydrogen sulfide, and 0.145 moles of carbon disulfide are introduced into a 2.00 liter reaction vessel. When the mixture reaches equilibrium, the concentration of hydrogen gas is found to be 0.56 M. What is the value of the equilibrium constant for this reaction under these conditions? (10 points)

	CH_4	$2\text{H}_2\text{S}$	CS_2	4H_2
I	3/2	2.2/2	.145/2	0
C	↓ -x	↓ -2x	↑ +x	↑ +4x
E	1.5-x ?	1.1-2x ?	.145+x ?	4x 0.56

$$4x = 0.56$$

$$x = 0.14 \text{ M}$$

$$K_{eq} = \frac{(0.56)^4 (0.145 + 0.14)}{(1.1 - 0.28)^2 (1.5 - 0.14)} = 0.022$$

2 pts for EQ
2 pts for K_{eq}
24 pts for ICE
2 pts for plug

10 for all
but
4x=0.56

10 no attempt to ICE

In a second experiment, 0.14 moles of methane, 0.28 moles of hydrogen sulfide, 0.14 moles of carbon disulfide, and 0.56 moles of hydrogen gas are combined in a 1.00 liter flask.

b) Would you expect this mixture to be at equilibrium? Please carefully justify your answer. (If you were unable to reach an answer for part (a), assume that K_c for this reaction = 0.0229.) (5 points)

$$Q = \frac{(0.56)^4 (0.14)}{(0.28)^2 (0.14)} = 1.254 \gg K_{eq} \quad \text{NOT AT EQUILIBRIUM (too much product)}$$

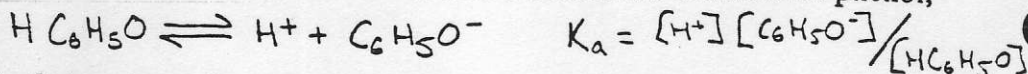
pts
answer
pts
reason

c) As the mixture maintains or moves toward equilibrium, would you expect the hydrogen sulfide concentration to increase, decrease, or stay the same? Please carefully justify your answer. (5 points)

Reaction will move to left to reduce Q. $[\text{H}_2\text{S}]$ will increase.

15 if say not match [] in (a)

The table in appendix D of your textbook indicates that the acid dissociation constant for phenol, $\text{HC}_6\text{H}_5\text{O}$, is 1.3×10^{-10} .



a) If 25 mmoles (millimoles) of phenol are dissolved in water to a final volume of 100.0 mL, what will be the concentrations of *all solution components* after equilibrium has been reached? (10 points)

2 pts →

$$\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^- \quad [\text{HA}]_0 = 25 \times 10^{-3} \text{ mol} / 0.1 \text{ L} = 0.25 \text{ M}$$

1 pts

I	0.25	-	-
C	↓	↑	↑
	-x	+x	+x
E	0.25-x	x	x

1 pt.

$$\rightarrow K_a = 1.3 \times 10^{-10} = \frac{x^2}{0.25-x} \quad \left. \begin{array}{l} x_1 = 0 \\ x_2 = 5.7 \times 10^{-6} \\ x_3 = 5.7 \times 10^{-6} \end{array} \right\} 2 \text{ pts.}$$

at eq, $[\text{HA}] \approx 0.25 \text{ M}$ $[\text{H}^+] = 5.7 \times 10^{-6} \text{ M}$
 $[\text{A}^-] = 5.7 \times 10^{-6} \text{ M}$ $[\text{OH}^-] = 10^{-14} / [\text{H}^+] = 1.7 \times 10^{-9}$ } 2 pts.

b) What will be the pH of this solution? Is this solution acidic, basic, or neutral? (5 points)

$\text{pH} = -\log [\text{H}^+] = 5.24$ This is (weakly) acidic.

3 pts.

2 pts.

c) What is the percent ionization of phenol under these conditions? Would you classify phenol as a strong acid, weak acid, strong base, or weak base? (5 points)

$$\text{Percent ionization} = \frac{[\text{ionized}]}{[\text{total}]} = \frac{[\text{A}^-]}{[\text{HA}]_0} = \frac{5.7 \times 10^{-6}}{0.25} = 2.3 \times 10^{-3} \%$$

4 pts.

Phenol is a weak acid } 2 pts.

* if comment effectively on low % ion but no #

2. Sodium hypochlorite (NaOCl) forms a weakly basic solution in water. Hypochlorous acid (HOCl) forms a weakly acidic solution in water with a K_a of 3.0×10^{-8} at 25°C .

a) What is value of the K_b for hypochlorite? (3 points)

$$K_b = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{3 \times 10^{-8}} = 3.3 \times 10^{-7}$$

* next time, have write out equilibrium as well!

b) If 0.32 moles of sodium hypochlorite are dissolved in 2.00 liters of water, what do you predict to be the resulting pH? (8 points)

-4 for wrong K + wrong



I	0.16	0	0
C	-x	+x	+x
E	0.16-x	x	x

$$K_b = 3.3 \times 10^{-7} = \frac{x^2}{0.16-x}$$

$$x_1 = 0$$

$$x_2 = 2.31 \times 10^{-4} \text{ M} = [\text{OH}^-]$$

$$[\text{H}^+] = 4.33 \times 10^{-11} \text{ M}$$

$$\text{pH} = 10.36$$

c) You wish to alter the pH of the solution in part (b) by adding 0.18 moles of one of the following: sodium chloride or hydrogen chloride. Will addition of either (or both) of these alter the pH? Please explain your answer. (6 points)

NaCl: no change — neither Na^+ or Cl^- will alter this equilibrium substantially.

HCl: this is a strong acid; it will have the effect of converting OCl^- to HOCl + pH will decrease.

-2 no NaCl

d) For the substance that you picked in part (c), please tell me what you expect the new pH to be. (If you are unsure of your answer to part (b), you may assume that the correct pH was 9.0. If you are unsure of your answer to part (c), try it for hydrogen chloride.) (10 points)

	OCl^-	H^+	HOCl
before	0.32 mole	0.18 mole	3.3×10^{-7}
after	0.14	0	0.18

4 pts

4 pts 2 parts, regardless of:



I	0.14	0.18	0
C	-	+x	+x
E	$\frac{0.14-x}{2}$	$\frac{0.18+x}{2}$	x

$$K_b = 3.3 \times 10^{-7} = \frac{x(0.09+x)}{(0.07-x)}$$

$$x_1 = 0$$

$$x_2 = 2.59 \times 10^{-7} = [\text{OH}^-]$$

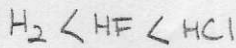
$$[\text{H}^+] = 3.86 \times 10^{-8}$$

$$\text{pH} = 7.4 \text{ (Yes, it went down)}$$

3. Please rank the following substances in terms of INCREASING acidity, and briefly explain your logic for each choice. (4 points each for a-c, 1 point for part d)

a) H_2 , HF, and HCl.

↳ 2 pts for trend
2 pts for rationale → observation vs explanation -1



(with increasing size of X in HX)

decreasing H-X bond strength from HF to HCl[↑] makes it easier for H⁺ to leave.

H_2 is not acidic.

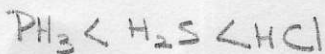
b) Phosphoric acid (H_3PO_4), perchloric acid ($HClO_4$), phosphorous acid (H_3PO_3), and sulfuric acid (H_2SO_4).



Increasing EN of central atom increases stability of conj. base

Increasing #Oxygen atoms increases stability of conj base

c) H_2S , HCl, and PH_3 .



Increasing EN of X increases polarity of H-X bond, making it easier for H⁺ to leave.

d) Here's your bonus point, as promised. But there's no free lunch, so please tell me: on average, how many hours of sleep would you estimate that you get each night (during the week/during the weekend)?

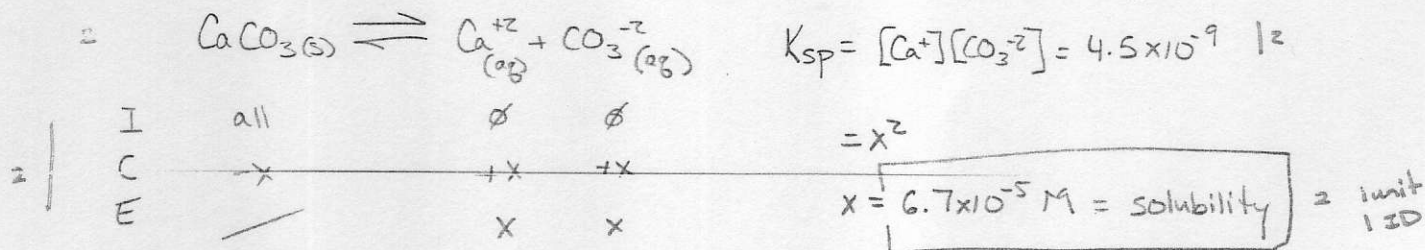
week								
6.5	6	6	6.5	5	6.5	6.5	6.5	7
6	6	6.5	6	7	7	6.5	6	6
7.5	7	4.5	7	5.5	5.5	7	5.5	7.5
6.5	4	7.5	6.5	5.5	6	5.5	5	7
6	6.5	5	6.5	7	5.5	5	7	



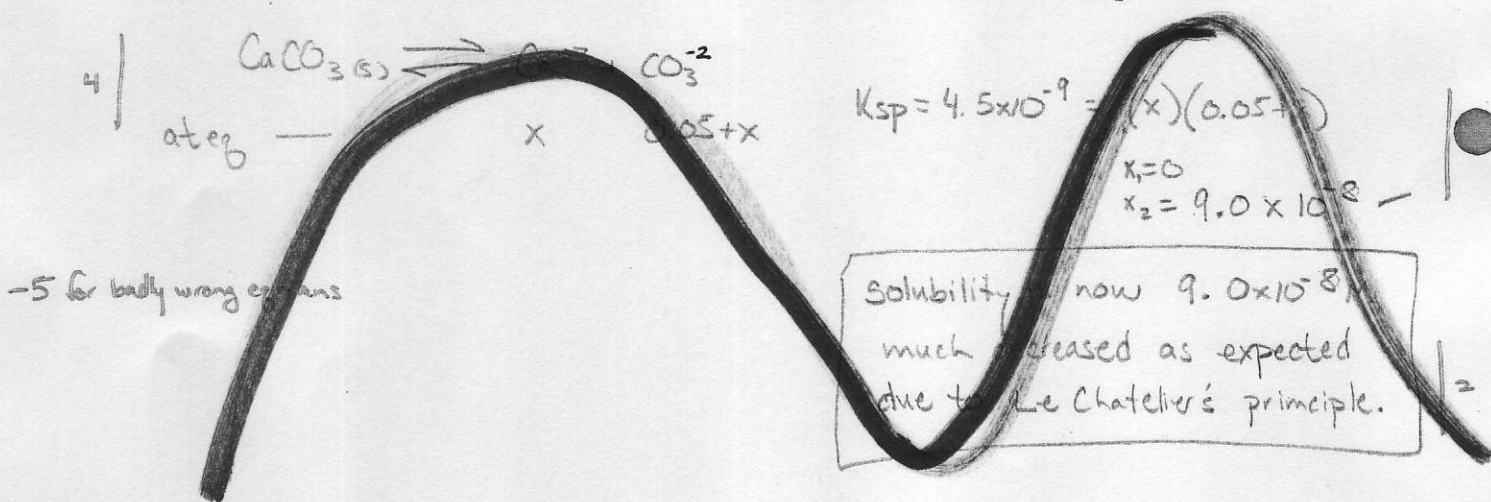
weekend								
7.5	6	10	6.5	7.5	10	8.5	9	8
6	6	8.5	8	8	9	6.5	6	7
8.5	10	7	8	8	10	9	5.5	9
7	6	10	8.5	9.5	8	7	7	-

4. Calcium carbonate is a common substance, showing up in our everyday lives as chalk, limestone, flowstone formations in caves, hard-water scale in tubs and hot water heaters, and as a major component of eggshells. The solubility product constant for calcium carbonate is 4.5×10^{-9} at 25°C .

a) What is the molar solubility of calcium carbonate in water at this temperature? (8 points)



b) What is the molar solubility of calcium carbonate in 0.050 M aqueous potassium carbonate at this temperature? Is this outcome relative to part (a) what you would predict? (8 points)



c) In equilibrium terms, how can you explain the increased solubility of calcium carbonate in acidic solutions? Please be specific and thorough in your answer. (4 points)

Acidic solutions, by definition, have high $[\text{H}^+]$

1. H^+ combines w/ CO_3^{2-} to form HCO_3^- and H_2CO_3 .

1. This reduces $[\text{CO}_3^{2-}]$.

By Le Chatelier, this pulls the equilibrium to the right, increasing solubility.