1. (20 pts; 2 points each) True or false: Place an X in the appropriate column

Statement	True	False
The pH at the half-equivalence point is always the average of the pK_a at the beginning of a titration and at the equivalence point.		X
The histidine side chain is neutral at pH 4.		X
At equilibrium the rates of the forward and reverse reactions are both zero.		X
The Henderson-Hasselbach equation is not correct when $[A^-]$ is too large.		X
When we add equations we add equilibrium constants.		X
The buffering range for a weak acid is between the pK_a and $pK_a + 2$, but not below the pK_a.		X
K_p and K_c are equal to each other if there are no gases involved in the equilibrium.	X	
The percent dissociation of a weak acid decreases as its concentration decreases.		X
In multiple equilibrium problems, all equilibria must be satisfied.	X	
The equilibrium constant of a reverse reaction is the reciprocal of the equilibrium constant of the corresponding forward reaction.	X	

Score for the page_____

2. (24 pts) Chemical Equilibria

(a; 9 pts) State LeChatelier's principle. Define the reaction quotient Q, and give the equivalent of LeChatelier's principle in the language of thermodynamics.

(+3) When stress is placed on an equilibrium, the equilibrium shifts to relieve the stress

(+3) $Q = \frac{[\text{products}]}{[\text{reactants}]}$ → each raised to the power of its stoichiometric coefficient, not necessarily at equilibrium

(+3) Q approaches K as equilibrium is established

(b; 3 pts) Write the K_c expression for the following reaction:

$$BaSO_4\,(s) \rightleftharpoons Ba^{2+}\,(aq) + SO_4^{2-}(aq)$$

(+3) $K_c = [Ba^{2+}][SO_4^{2-}] / (BaSO_4) \; (= K_{sp})$ +2

(c; 2 pts) Does the amount of dissolved barium ion depend on the amount of solid barium sulfate sitting at the bottom of the beaker? Circle one: YES (NO)

(+2)

(d; 6 pts) It turns out that the numerical value of K_c is 1.1×10^{-10}. The small value for K_c for some sulfate salts is the basis of selective precipitations in quantitative analysis, in which, for example, one can use a standardized sodium sulfate solution to measure the barium ion concentration in a test sample. Calculate the concentration of barium ion in solution if the $[SO_4^{2-}]$ is 75 mM. If the initial barium ion concentration before precipitation with $NaSO_4$ was 125 mM, what percentage of the barium ion remains in solution?

$$[Ba^{2+}] = \frac{K_c}{[SO_4^{2-}]} = \frac{1.1\times10^{-10}\,(M^2)}{0.075\,(M)} = 1.47\times10^{-9}\,M$$ (or 1.5×10^{-9} M)

1.47 × 10⁻⁶ mM

(+2)

$$\%\text{ in Solution} = \frac{1.47\times10^{-9}\,M}{125\,mM} \times 100 = 1.2\times10^{-6}\,\%$$ [i.e. just about none!]

(+2)

0.125 M

$$\frac{1.47\times10^{-9}\,M}{0.125\,M} \times 100\% = 1.2\times10^{-6}\%$$

1.2 × 10⁻⁶ %

Score for the page_____

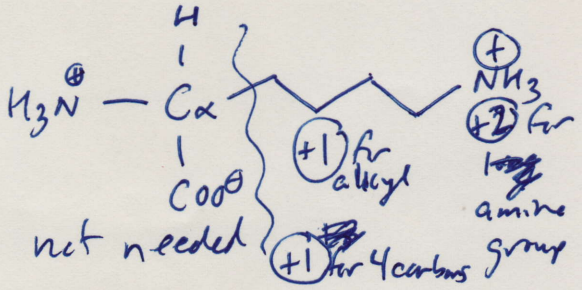
(e; 4 pts) Why do we use $NaSO_4$ instead of sulfuric acid for the barium precipitation (other than safety)?

$[SO_4^{2-}]$ (+2) in sulfuric acid is low - it's mostly HSO_4^- (+1), so the precipitation is less efficient (+2) (BaSO4 is actually soluble in hot sulfuric acid)

Adds up to 5 - max points = 4

3. (18 pts) Biological Applications

(a; 6 pts) Draw the structure of the Lysine side chain at pH 7 and give its approximate pK_a.



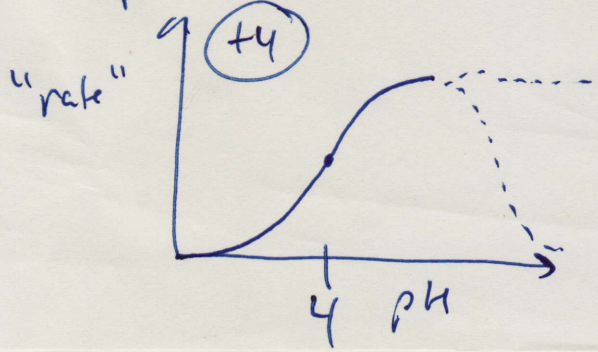
pKa = 10.5
(+2) for 10, 10.5, or 11

(b; 12 pts) Explain why measuring the pH dependence of an enzymatic reaction is a useful probe into mechanism. Explain why, however, the experiment offers only a guide to identifying the active site residue type(s). As a concrete example, explain how a pH curve might suggest but not prove that a ~~lysine~~ Asp or Glu residue is involved in catalysis.

(+4) - The pH dependence reflects mechanistic steps in which a proton must be abstracted or donated. The pH dependence tells us the pKa's of the residues that are being titrated as the reaction fails.

(+4) - The pKa's in active sites, however, can be wildly different from the pKa's of free amino acid side chains, so one can't simply say that a pKa of 4 means aspartate.

pH curve: Let's imagine that a reaction requires a deprotonated $Asp^{\ominus}$ residue to act as a base. The curve to the left would result. But it could also be a histidine with an altered pKa that needs to be protonated.



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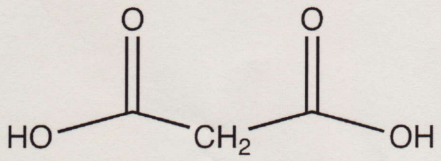
4. (38 pts) Acid-base chemistry and multiple equilibria

Consider the diprotic acid malonic acid, with pK_a's 2.83 and 5.89. (Malonic acid is an inhibitor of the important metabolic enzyme succinate dehydrogenase.)

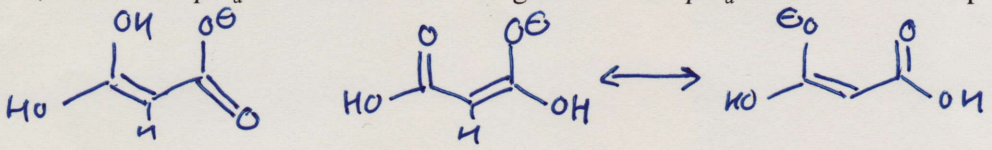


(a; 8 pts) The first pKa is very low relative to a typical carboxylic acid like acetic acid, $pK_a = 4.75$. This means that malonic acid is a (circle one): stronger acid or a weaker acid than acetic acid. Sketch a structure that rationalizes this (three acceptable possible answers). On the other hand, the second pK_a of malonic acid is higher than the pK_a of acetic acid. Explain why.

+2

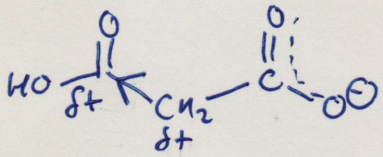
+3 for any one, +1 for just trying

Resonance:



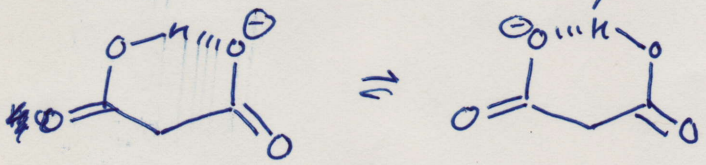
Dubious but acceptable

Inductive effect:



electron-withdrawing substituent stabilizes ⊖ charge need not be on adjacent carbon

H-bonding:



H-bonding stabilizes ⊖ charge

+3

– Removal of the second proton is always harder because we are separating H^+ from an anion

(b; 4 pts) Why can we ignore the second pK_a when calculating the pH of a malonic acid solution?

+4 for either or

– The dissociation of the first proton suppresses dissociation of the second

– The pH resulting from the 1st ionization is $<< pK_{a_2}$

(c; 6 pts) Calculate the pH of 0.150 M malonic acid, assuming (dubiously) that "x" << 0.150 M.

$H_2M \rightleftharpoons HM^- + H^+ \quad K_{a_1} = 10^{-2.83} = 1.48\times10^{-3}$] +1 for setup

	H_2M	HM^-	H^+
I	0.150	0	0
C	$-x$	$+x$	$+x$
E	~~0.150~~ $0.150-x$	$+x$	$+x$

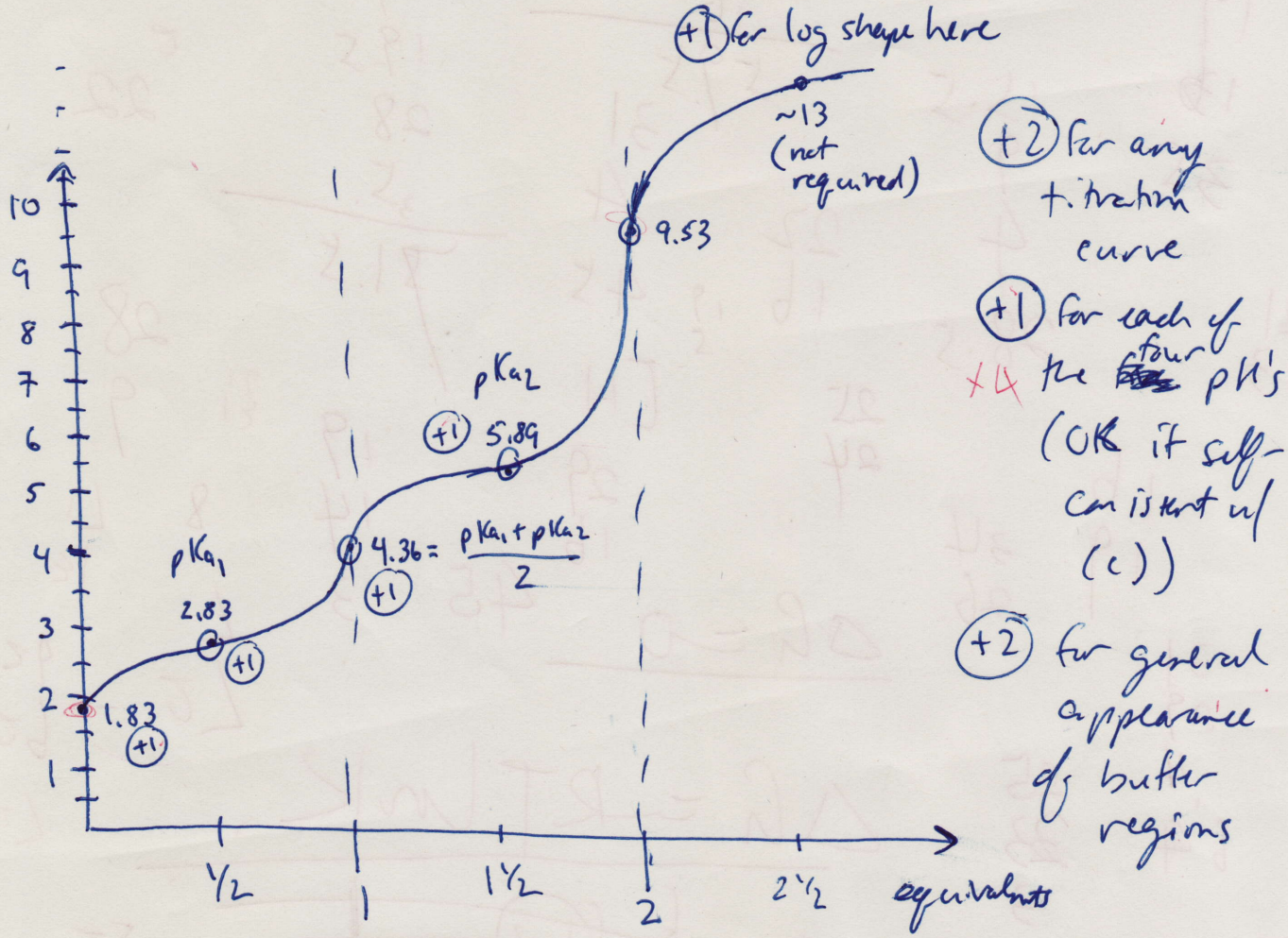
$\frac{x^2}{0.150-x} \approx \frac{x^2}{0.150} = 1.48\times10^{-3}$ +2

$x = 1.49\times10^{-2}$ +1

$pH = -\log(x) = 1.83$ +2

Score for the page_____

(d; 9 pts) Sketch a curve of the pH as we titrate 0.150 M malonic acid with NaOH, ignoring dilution. Specify the pH for the beginning (the number you just calculated in *c*), the two half-equivalence points, and the two equivalence points (the second one is at pH = 9.53).



Score for the page 9

(e; 4 pts) We did not learn to calculate the exact pH for diprotic acid titrations, but we do know how to set up the problem. For any point on a titration of malonic acid H_2M being converted to HM^- and M^{2-} with added NaOH, we know the $[Na^+]$ and we would like to calculate the concentrations of five other chemical species. One is hydroxide. Write down the other four. (Not a trick question)

$[H^+]$, $[H_2M]$, $[HM^-]$, $[M^{2-}]$ (+4) pts (simme)

(f; 7 pts) We need five equations to solve the problem. Two of them are the two K_a relationships for the first and second acid dissociation equilibria. Write down the last equilibrium relationship needed and the two conservation equations that we need to have five equations. Hint: the total charge of the solution is zero.

(+2) $K_w = [H^+][HO^-]$ (+1) if $K_w = \frac{[H^+][OH^-]}{[H_2O]}$

(+2) $C_o = [H_2M] + [HM^-] + [M^{2-}]$

constant total [ ] of malonate (+2) if the "2" is missing

(+3) $[Na^+] + [H^+] = [HM^-] + 2[M^{2-}] + [HO^-]$ (+2) if $-2[M^{2-}]$ instead

conservation of total charge (solution must be neutral)

Page	Score
2	/20
3	/20
4	/22
5	/18
6	/9
7	/11
Total	**/100**

Score for the page_____