Acids & Bases

Answers and Explanations

1. A

Within the subject of acids and bases, we will most often be situated within the Brønsted-Lowry system, where acid base activity is conceived in terms of proton exchange. However, the Lewis system is a useful conceptual framework. A Lewis base is any substance that can donate a pair of nonbonding electrons. A Lewis base is an electron-pair donor. Of the answer choices, all of them possess a nonbonded pair of electrons except for methane.

2. C

K_a increases with increasing dissociation of the acid. Therefore, the smaller K_a the weaker the acid.

$$HA \rightleftharpoons A^- + H^+$$

$$K_a = \frac{[A^-]\,[H^+]}{[HA]}$$

3. B

When you ask about the strength of an acid you are asking about is the position of this equilibrium.

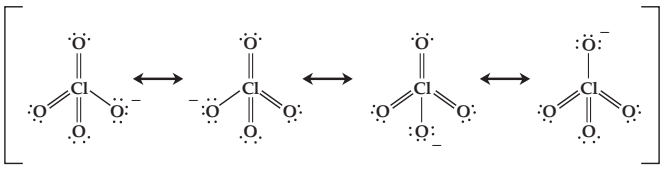
$$HA \rightleftharpoons A^- + H^+$$

The stronger the acid, the further to the right the position of this equilibrium. Remember that the position of an equilibrium is determined by the standard free energy change.

$$K = e^{\frac{-\Delta G^\circ}{RT}}$$

For strong acids, like perchloric acid, the standard free energy change is negative. For a weak acid like hypochlorous acid ($K_a = 3.2 \times 10^{-8}$), the standard free energy change is positive.

In summary, the question of why an acid is strong is really the question of why the standard free energy change of dissociation is negative. The answer can often be found in the stability of the conjugate base. For perchloric acid, the answer is that the conjugate base, perchlorate, is extremely resonance stabilized. Below are its four most prominent resonance forms.



The acidity of the many oxygen acids of nonmetals can be understood in terms of the resonance stabilization of the conjugate base, ie. sulfuric acid, phosphoric acid, carbonic acid, etc.

4. C

Just as with pH, pK_a is basically a way to write a number more conveniently. It converts a number in scientific notation with a negative exponent into a much simpler form. It goes back to a time when scientific notation was a big typographical hassle, but then the system then took on a life of its own, and it has become a valuable way to conceptualize things.

$$pK_a = -\log K_a$$

To understand how to take the pK_a of a number, firstly, remember the following about logarithms.

$$\log (ab) = \log (a) + \log (b)$$

So our problem becomes

$$pK_a = -\log (3.2 \times 10^{-8}) = -[\log (3.2) + \log (10^{-8})]$$

$$pK_a = -[\log (3.2) - 8]$$

$$pK_a = 8 - \log (3.2)$$

At this stage, for log(3.2) you might ask yourself 'to what power do I raise the number 10 to get 3.2?' This is near to the square root of 10, so ½ then. Or you might use the linear interpolation shortcut and say log (3.2) ~ 0.32. For the MCAT, that's usually the way. Make the negative exponent a positive whole number and subtract ⅒ of the coefficient from this whole number.

$$pK_a = -\log (3.2 \times 10^{-8}) \sim 8 - 0.3 \sim 7.7$$

6. C

To determine the approximate pH of our solution at equilibrium, we will start with the expression describing that equilibrium state, the K_a of HCN.

$$\frac{[A^-]\,[H^+]}{[HA]} = K_a$$

$$\frac{[CN^-]\,[H^+]}{[HCN]} = 4.9 \times 10^{-10}$$

There is a longer, more exact way to do this, and there is a shorter, more approximate way. The longer way takes into account the H^+ ions already present in pure water, and it also assumes that the amount of the weak acid which dissociates is significant compared to the concentration of undissociated weak acid. This longer way involves a number of steps which will lead ultimately to the quadratic equation. All quantitative MCAT questions are designed to be solved more quickly than this. If you are asked to do this classic Chem 101 problem on the MCAT, the question stem will almost certainly say 'approximate pH' letting you know you have permission to use the shorter method.

For the shorter method, we make two assumptions. When the acid dissociates, for each mole of protons liberated, so also is a mole of conjugate base.

$$HA \rightleftharpoons A^- + H^+$$

Ignoring the already 10^{-7} M H^+ in the water before admixture, our first assumption is as follows.

$$[H^+] \approx [A^-]$$

Additionally, we are going to assume that the concentration of acid which dissociates is very small compared to the initial concentration added.

$$[HA]_{equilibrium} \approx [HA]_0$$

In our problem we added approximately two moles of HCN (MW = 27g mol^{-1}) to 20L water making approximately 20L solution, so our initial concentration, $[HA]_0 \sim 0.1M$.

Now we can restate our expression for K_a using our approximations.

$$\frac{[CN^-]\,[H^+]}{[HCN]} = 4.9 \times 10^{-10}$$

$$\frac{[H^+]^2}{0.1\ M} = 4.9 \times 10^{-10}$$

$$\frac{[H^+]^2}{1 \times 10^{-1}\ M} = 4.9 \times 10^{-10}$$

$$[H^+]^2 = 4.9 \times 10^{-11}$$

To take the square root of a number in scientific notation, you need the exponent to be an even number.

$$[H^+]^2 = 49 \times 10^{-12}$$

$$[H^+] = 7 \times 10^{-6}$$

Now use your method for approximating pH when given $[H^+]$ in scientific notation. Make the negative exponent a positive whole number and subtract ⅒ of the coefficient from this whole number.

$$pH = -\log (7 \times 10^{-6}) \sim 6 - 0.7 \sim 5.3$$

7. C

With this kind of problem, it's natural not to see the whole problem solving algorithm from start to finish in your head. Start working with what you know. Think with your pencil, and let the problem unfold. A big part of the art of this kind of thing is learning to trust yourself to just get started. We can see it's useful to convert the pH of the solution into hydrogen ion concentration, so let's do that.

$$pH = 1$$

$$-\log[H^+] = 1$$

$$[H^+] = 10^{-1}$$

Now we can start rolling out conversion factors. Lay it out stepwise and work towards your goal.

We can multiply the volume of the solution times the H^+ concentration. This would give us the number of moles of H^+ in the solution.

$$(2\text{ L})\,\frac{(1\times10^{-1}\text{ mole H}^+)}{\text{L}}$$

We were told it is a diprotic strong acid. This gives us a stoichiometric ratio to convert our moles of H^+ into moles of our acid.

$$(2\text{ L})\,\frac{(1\times10^{-1}\text{ mole H}^+)}{\text{L}}\,\frac{(1\text{ mole acid})}{(2\text{ mol H}^+)}=10^{-1}\text{ mole acid}$$

So now we know that our 10g of acid equals 0.1 mole, so we can determine the molecular weight.

$$\frac{10\text{g}}{0.1\text{ mol}}=100\,\frac{\text{g}}{\text{mol}}$$

8. A

To find $[H^+]$ we can begin by determining the pH, given that pOH = 3.5.

$$\text{pH}+\text{pOH}=14$$

$$\text{pH}=10.5$$

$$-\log[H^+]=10.5$$

$$\log[H^+]=-10.5$$

$$[H^+]=10^{-10.5}$$

$$[H^+]=(10^{0.5})(10^{-11})$$

$$[H^+]=3.2\times10^{-11}\text{ M}$$

Though the mathematical operations to move from pH to $[H^+]$ are useful to see, once it's determined that the pH is 10.5, it's possible to solve the problem by inspecting the answers because there's only once choice with $[H^+]$ between 10^{-11} and 10^{-10}.

9. C

Titration of an Arrhenius acid with an Arrhenius base produces a salt and water.

$$NaOH + HCl \rightharpoonup NaCl + H_2O$$

The titration described in the question stem yielded 5.9g NaCl (MW 59g). 5.9g equals 0.1 mol.

$$5.9\text{ g}\,\frac{1\text{ mol}}{59\text{ g}}=0.1\text{ mol}$$

From the stoichiometric ratio in the titration reaction, it can be seen that if 0.1 mol NaCl was produced, 0.1 mol NaOH was consumed. Therefore the initial concentration was 2.0M.

$$\frac{0.1\text{ mol}}{0.05\text{ L}}=2.0\text{ M}$$

Because one mole of NaOH produces one mole of OH^-, one mole represents one equivalent in titration. In other words, a 2.0M solution of NaOH is also 2.0N.

10. A

The equivalence point in a titration of acid with base is reached when you have added exactly as many equivalents of base as acid. This titration has reached the equivalency point.

$$N_{\text{acid}}V_{\text{acid}}=N_{\text{base}}V_{\text{base}}$$

$$(1\text{ N})(2\text{ L})=(0.5\text{ L})(4\text{ N})$$

Just because you have reached the equivalency point in a titration of an acid with a base does not mean the pH in the solution is neutral. You have to ask yourself what is actually in the beaker. In this case, we are titrating a strong acid with a strong base.

$$HCl + NH_4OH \rightharpoonup NH_4Cl + H_2O$$

Normally, one would expect the titration of a strong acid with a strong base to yield a neutral solution at equivalency, but the salt forming in this case is ammonium chloride, which is a weak acid.

11. B

At equivalency this titration will yield a solution of sodium nitrate. A sodium nitrate solution has a neutral pH.

$$HNO_3 + NaOH \rightharpoonup NaNO_3 + H_2O$$

A pH indicator is a weak acid – weak base pair (HI and I^-) where each of these is a different color. To interpret the behavior of an indicator when its color change occurs, it's helpful to see it within the framework of the Henderson-Hasselbalch equation.

$$pH = pK_a + \log\left(\frac{[I^-]}{[HI]}\right)$$

Using the Henderson-Hasselbalch equation in the context of a buffer solution, we see the ratio of the weak acid : weak base concentrations as the independent variable determining the pH of the solution. In the case of an indicator, however, we flip the script and think of the pH controlling the ratio of $[I^-]$ and [HI] instead of vice versa. (This is also how you should think of the state of ionization of biomolecules. Physiological pH dictates that an aspartate side chain is a reliable negative, for example.)

To choose an indicator, you want its pK_a to be as close to the pH of the equivalency point as possible. When the pH of the solution is a full unit below the pK_a of the indicator, the [HI]:$[I^-]$ ratio will be 10:1 and the solution will be one color. When the pH of the solution is a full unit above the pK_a of the indicator, the [HI]:$[I^-]$ ratio will be 1:10 and the solution will be a different color. If pK_a of the indicator is near to the pH of the equivalency point, this color change will occur as the pH sweeps across the equivalency point.

Because the equivalency point in our titration is a sodium nitrate solution with a neutral pH (pH = 7), the best indicator for this titration would be p-Nitrophenol (pK_a 7.2).

12. B

A buffer solution is a solution of a weak acid and its conjugate base. Buffer solutions stabilize the pH near the pK_a of the weak acid. A buffer absorbs excess protons or hydroxide into the equilibrium between the weak acid and weak base. To determine the pH of a buffer solution, we use the Henderson-Hasselbalch equation.

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

The first step is to convert the K_a of carbonic acid into its pK_a. On the MCAT feel free to use the approximation method. Make the negative exponent a positive whole number and subtract ⅒ of the coefficient from this whole number. This will get us close enough for the MCAT.

$$pK_a = -\log(4.4 \times 10^{-7}) \sim 7 - 0.44 \sim 6.6$$

If the concentration of the weak acid in a buffer is ten times the concentration of the base, the pH will be a full point lower than the pK_a of the acid.

$$pH \sim 6.6 + \log\left(\frac{0.1}{1.0}\right)$$

$$pH \sim 5.6$$

When you approximate pK_a, you shouldn't be surprised to land a few tenths of a point off in your answer. (The common logarithm of 4.4 is actually 0.64 not 0.44.) The MCAT almost never spaces quantitative answer choices near to one another. They want to encourage mental math.

13. C

HCl is a strong acid. K_2CO_3 is a strong electrolyte. Both will completely dissociate.

$$HCl \rightharpoonup Cl^- + H^+$$

$$K_2CO_3 \rightharpoonup 2K^+ + CO_3^{2-}$$

Excess H^+ will drive the carbonate to carbonic acid.

$$CO_3^{2-} + H^+ \rightharpoonup HCO_3^-$$

$$HCO_3^- + H^+ \rightharpoonup H_2CO_3$$

Carbonic acid decomposes to form carbon dioxide gas and water. This is one of the MCAT's favorite reactions.

$$H_2CO_3(aq) \rightharpoonup CO_2(g) + H_2O$$

14. D

It is axiomatic in general chemistry that nonmetal oxides react with water to form acids, and metal oxides react with water to form bases. Of our choices, three are nonmetal oxides. These will form acids in water.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$SO_2 + H_2O \rightleftharpoons H_2SO_3$$

$$P_4O_{10} + 6H_2O \rightleftharpoons 4H_3PO_4$$

Calcium oxide is a metal oxide. It forms a base in water.

$$CaO + H_2O \rightleftharpoons Ca(OH)_2$$

15. A

HF is the only hydrohalic acid that isn't classified as a strong acid. When HF dissociates the hydronium ion remains attached to F^-, so HF is functionally a weak acid.

16. A

As a general rule with oxygen acids, the greater the number of oxygens around the central atom, the stronger the acid. Not only will there be greater inductive pull from the oxygens polarizing the O–H bond, there will be more resonance forms to stabilize the conjugate base.

17. C

A crucial application of the Henderson-Hasselbalch framework in biochemistry is to understand how physiological pH (7.4) dictates the state of ionization of biomolecules. The ratio of protonated to unprotonated forms will adjust to the pH.

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

Substituting the values for the lysine side-chain, we can see that at physiological pH, lysine will be protonated at approximately 1000:1 ratio.

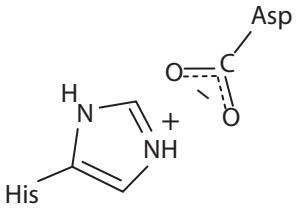
$$7.4 = 10.5 + \log\left(\frac{[lys\text{–}NH_2]}{[lys\text{–}NH_3^+]}\right)$$

$$\log\left(\frac{[lys\text{–}NH_2]}{[lys\text{–}NH_3^+]}\right) = -3.1$$

$$\frac{[lys\text{–}NH_2]}{[lys\text{–}NH_3^+]} = \frac{1}{1000}$$

18. A

The salt bridge stabilizes acid form of the histidine residue and the base form of aspartate.



If the acid form of histidine is more stable, the surroundings will push protons onto histidine more easily. The histidine will more likely be protonated. The pK_a of the side chain of a free histidine in aqueous solution is 6.0. At physiological pH this would mean only 1:25, approximately, are protonated. This salt bridge stabilizing the conjugate acid has raised the pK_a above physiological pH, so now the majority of the time a histidine residues will be protonated.

The same logic applies to the lowering of the pK_a of the aspartate residue. The salt bridge stabilizes the carboxylate form. However, this is not so significant biochemically because aspartate is already a reliable negative. The pK_a of the side chain of a free aspartate is 3.8. In other words, at physiological pH, nearly all aspartate side chains are deprotonated, so lowering the pK_a even further produces no big effect.

Conversely, the change in the pK_a of the histidine is very significant biochemically and physiologically. It's the molecular basis for the Bohr effect, the decrease in the affinity of hemoglobin for oxygen at lower pH. The deoxygenated form is stabilized in the tissues where CO_2 production has lowered pH. Oxygen unloads as protons load onto hemoglobin.

19. B

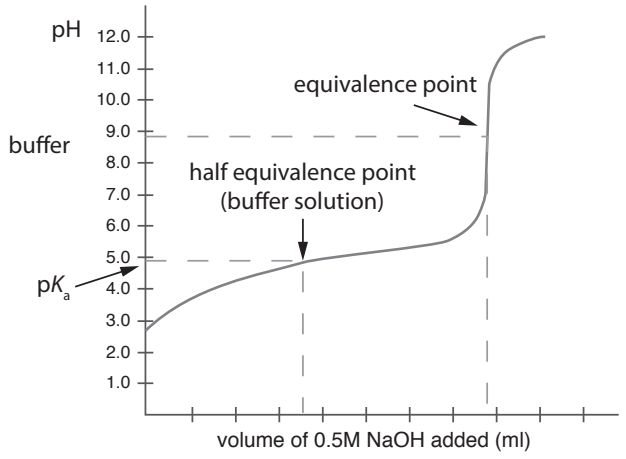
The titration of a weak acid with a strong base involves the strong base converting the weak acid into weak base. For example, if we were titrating acetic acid with sodium hydroxide, we would be forming sodium acetate.

$$HC_2H_3O_2 + NaOH \rightharpoonup NaC_2H_3O_2 + H_2O$$

At the equivalence point we would have added exactly as many equivalents of NaOH as $HC_2H_3O_2$, and we would have produced a solution of $NaC_2H_3O_2$. Up to that point, though, our solution would constitute a mixture of $HC_2H_3O_2$ and $NaC_2H_3O_2$. A solution which is a mixture of a weak acid and its conjugate base is a buffer solution. We can see from the Henderson-Hasselbalch equation that at the half equivalency point, when the concentrations of the weak acid and base are equal, the pH of the solution would be equal to the pK_a of the weak acid.

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

In the titration of a weak acid with a strong base, you can determine the pK_a of the weak acid by inspection of the titration curve. The pH halfway to the equivalence point equals the pK_a.



20. C

The answer choices exemplify a commonly employed format representing amino acid substitutions. 'A123D' signifies that an alanine was changed to aspartate at position 123 in the primary structure.

The isoelectric point, pI, of a protein, is the pH at which the most likely state of ionization of the protein is electrically neutral, so the protein does not migrate in an electric field if the pH of its solution environment equals its isoelectric point.

It helps to understand isoelectric point to picture an acidic solution environment as a kind of proton pressure onto the protein and a basic solution environment as a kind of pull that removes protons from the protein. A protein with a large proportion of aspartate and glutamate will be negatively charged at neutral pH. It will have a low isoelectric point because it requires an acidic pH to push protons onto the protein and make those negative charges neutral. Likewise, a protein with a large proportion of lysine or arginine will have a high isoelectric point. It will be positively charged at neutral pH, and it requires the pH to be more basic to pull the protons off of those residues and render the protein neutrally charged.

Of our answer choices, the substitution that would be expected to produced the greatest decrease in the isoelectric point is K299E. We are removing a positively charged residue (K = lysine) and replacing it with a negatively charged residue (E = glutamate). Instead of pulling a proton off to neutralize the residue, we would have to push a proton on, so the isoelectric point will now be more acidic.

One thing to mention. If you missed this question because you don't know the single letter codes for the amino acids, it might be a good time to start hitting those, even if you haven't gotten to biochemistry in content review. The MCAT will give you a bad time if you don't know those backwards and forwards.