

Chapter 16 Worksheet 2 (ws16.2)
Understanding the shapes of acid-base titration curves

Neutralization Reactions go to Completion

Every acid-base reaction produces another acid and another base. A **neutralization reaction** is a reaction between an acid and a base that produces a **weaker** acid and a **weaker** base. Neutralization reactions usually have very large equilibrium constants (even if the acid and base are both weak) so they go to completion. Let's see why.

1. Write the balanced molecular and net ionic equations for the reaction of acetic acid with ammonia. Is this a neutralization reaction? (The table of K_a 's and K_b 's from ws15.1 is attached to this document.)

2. This reaction can be thought of as occurring in 3 steps:

Step 1: Ionization of acetic acid

Step 2: Ionization of ammonia

Step 3: Reaction of hydronium ion with hydroxide ion

Write the balanced equation for each step along with their equilibrium constants. Add the 3 reactions and calculate the equilibrium constant for the net reaction.

Step 1: $K_{eq} =$

Step 2: $K_{eq} =$

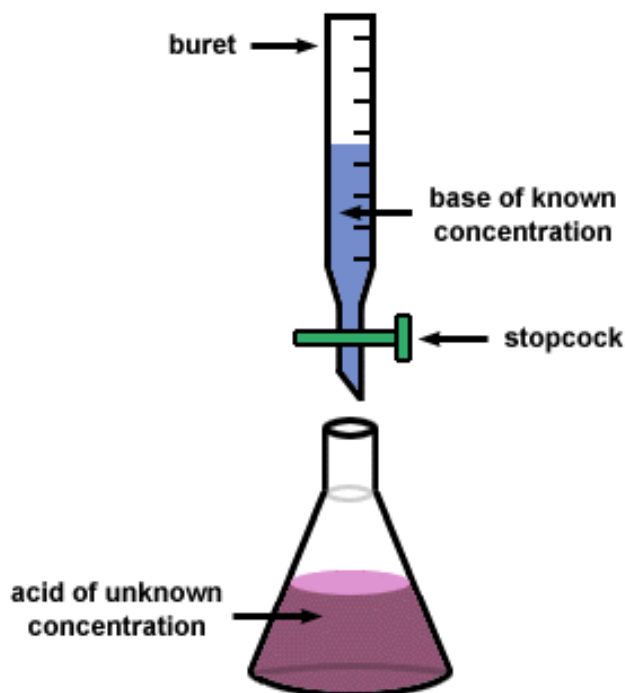
Step 3: _____ $K_{eq} =$

Net: $K_{eq} =$

3. Neutralization reactions do NOT usually result in a neutral pH ($pH = 7$). Recall that all acid-base reactions produce a salt and water. The reaction between a strong acid and strong base produces a(n) _____ salt. A strong acid and weak base produce a(n) _____ salt. A weak acid and strong base produce a(n) _____ salt. The pH after a neutralization reaction also depends on whether or not there is an excess reagent.

Acid-base titrations

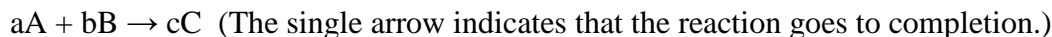
An acid-base titration is an analytical technique for determining the concentration of a dissolved acid or base and for determining the K_a for a weak acid. During a titration, a neutralization reaction is performed by slowly adding a solution of a base (**the titrant**) to a solution of an acid (or vice versa). Let's consider a titration of an acid solution whose concentration is unknown with a base whose concentration is known. (See figure.) The base is the titrant and it is added slowly to the acid.



When the titration begins, the base is the limiting reactant and is completely consumed (because neutralization reactions go to completion). Excess acid and the salt produced by the reaction are now in the flask. As the titration continues, more and more of the acid is consumed. Eventually all of the acid (and added base) is consumed. At this point, **stoichiometric amounts** of acid and base have been mixed and only a salt solution remains. This point is called the **equivalence point**. Given the volume of base added to reach the equivalence point, the known molarity of the base, and the stoichiometry of the reaction, you can calculate the number of moles of acid that was present initially. An indicator is used to determine when the equivalence point has been reached. If the titration is continued beyond the equivalence point, the base becomes the excess reagent and it simply accumulates (but no more salt is produced). If the acid is weak, the K_a can be determined by monitoring the pH during the titration. As demonstrated below, **the K_a is equal to the pH half-way to the equivalence point!**

Equivalence point calculations

Any reaction that goes to completion (not just neutralization reactions) can be performed as a titration. Consider the generic reaction:



At the equivalence point, stoichiometric amounts of A and B have been mixed and both have been completely consumed. Thus, at the equivalence point:

$$\frac{\text{moles of A reacted}}{\text{moles of B reacted}} = \frac{a}{b} \quad \left(\frac{a}{b} \text{ is called the } \mathbf{\text{stoichiometric ratio}}\right)$$

The equation can be re-written in terms of the molarity (M) and volume (V) of each reactant.

$$\frac{M_A V_A}{M_B V_B} = \frac{a}{b}$$

For most (but not all) acid-base reactions, the stoichiometric ratio is equal to one! The volume does NOT have to be in liters since the volume units will cancel as long as they are the same.

If you know all but one variable, you can calculate the value of the remaining variable. Most often, you are interested in determining one of the following:

- **The molarity of the acid or base being titrated.** Let's assume an acid is being titrated and a base is the titrant. In this case, you know the volume of the acid and the molarity of the base. You measure the volume of base required to reach the equivalence point. Since you know the stoichiometric ratio, the only unknown is the molarity of the acid.
- **The volume of titrant required to reach the equivalence point.** Again assume that you are titrating an acid with a base. In this case you know both the volume and molarity of the acid and the molarity of the base so the only unknown is the volume of base required to reach the equivalence point.

Do the following 2 problems on your own (use the next page). We will NOT do them in class.

1. It required 10.00 mL of 0.250 M NaOH to titrate 50.00 mL of HCl (to the equivalence point). What was the original concentration of the HCl? (Do the same problem but change NaOH to Ca(OH)₂. Do it again but react H₂SO₄ with NaOH. The stoichiometric ratios are no longer 1 to 1! Since NaOH is a strong base, **both** protons in sulfuric acid will be titrated.)
2. What volume of 0.100 M NaOH are required to reach the equivalence point if you titrate 25.00 mL of 0.500 M HCl? (Do the problem again but change the numbers or change the acid or base as above.)

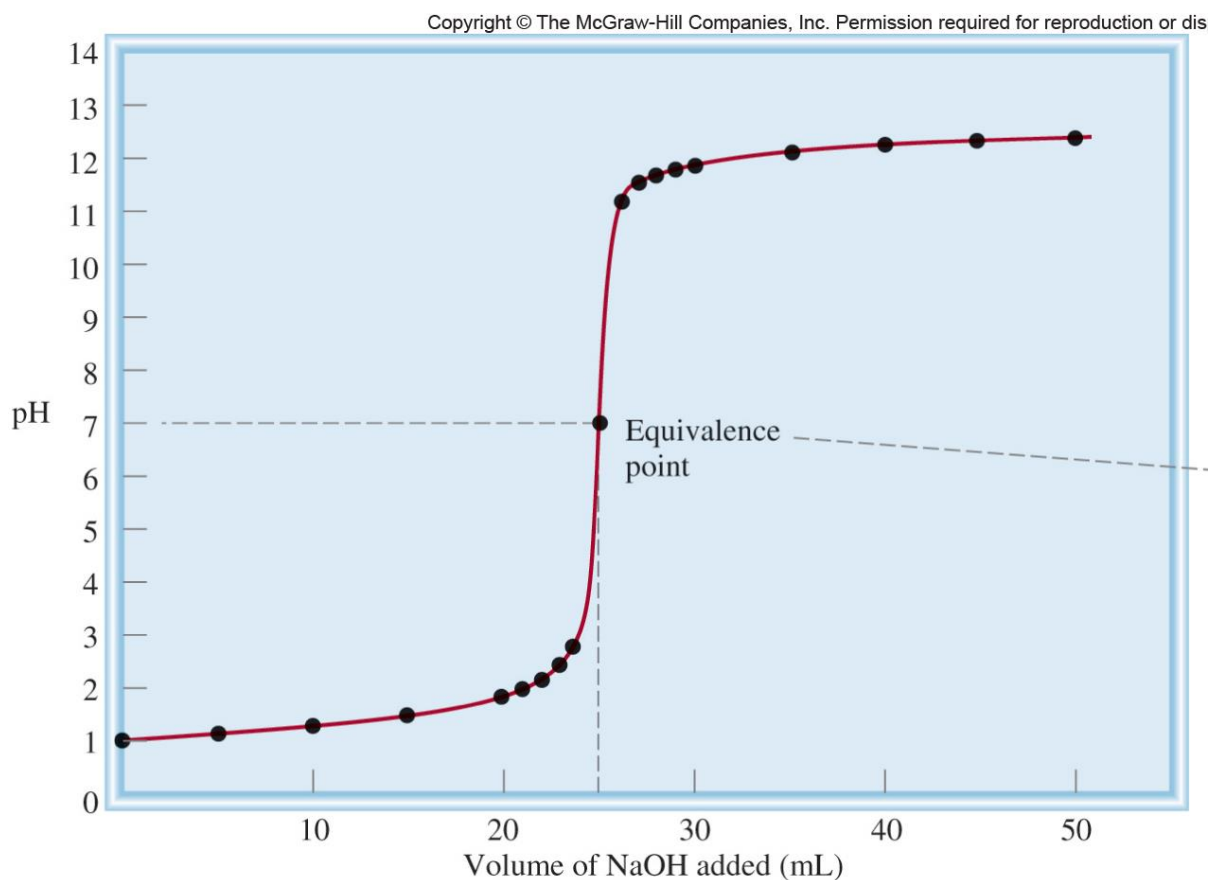
Understanding the shape of a titration curve

There are four phases of a titration:

- Phase 1: Before the titration begins
- Phase 2: Before the equivalence point
- Phase 3: At the equivalence point
- Phase 4: After the equivalence point

Label each titration curve below with the reaction that is occurring and the species present at each stage of the titration. For titrations involving a weak acid or weak base, label the region in which the solution is a buffer and the point where the $\text{pH} = \text{pK}_a$.

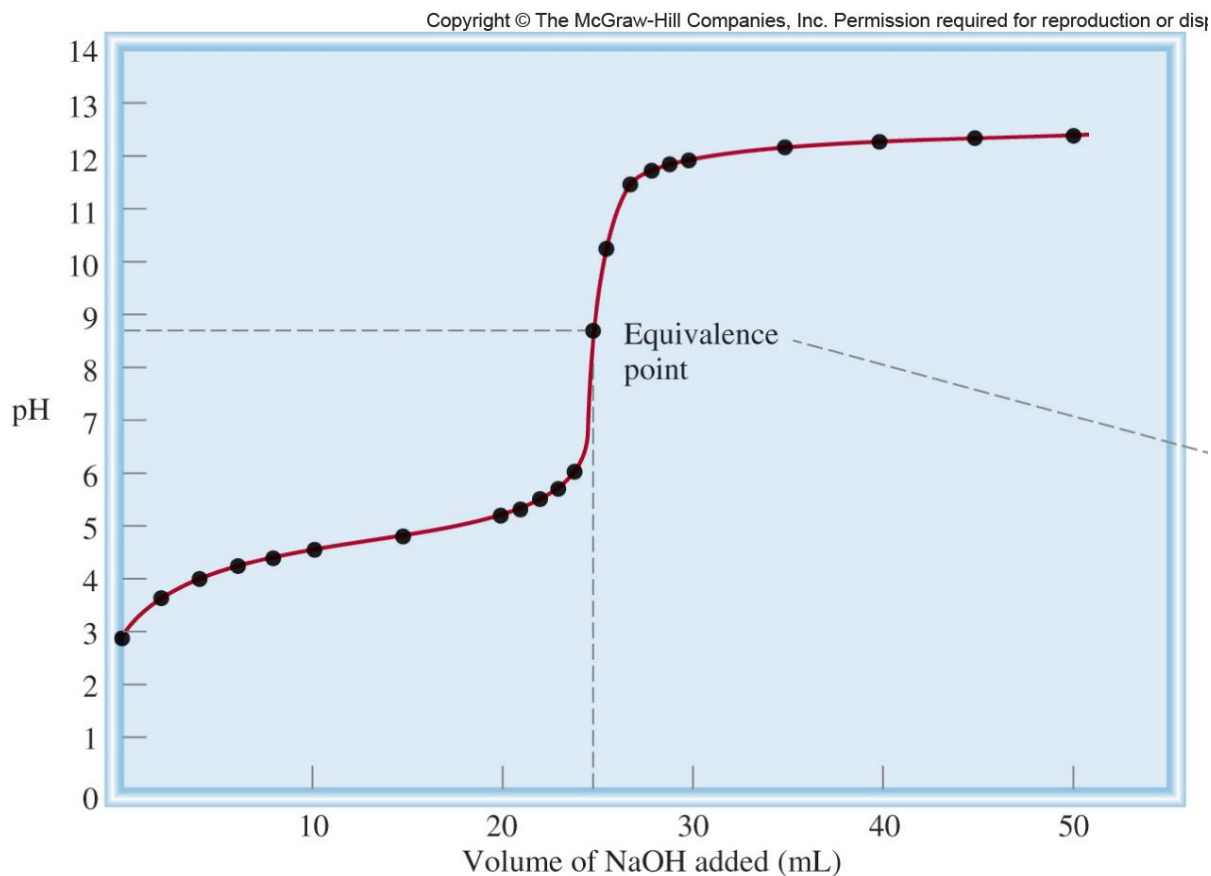
Titration of 25.00 mL of 0.100 M HCl with 0.100 M NaOH (strong acid, strong base):



Answer the following questions on the next page:

1. Calculate the initial pH.
2. Why is $\text{pH} = 7$ at the equivalence point?
3. Why does the pH rise slowly at first, very rapidly near the equivalence point, and slowly after the equivalence point?
4. Why does it require 25.00 mL of NaOH to reach the equivalence point?

Titration of 25.00 mL of 0.100 M CH₃COOH with 0.100 M NaOH (weak acid, strong base):

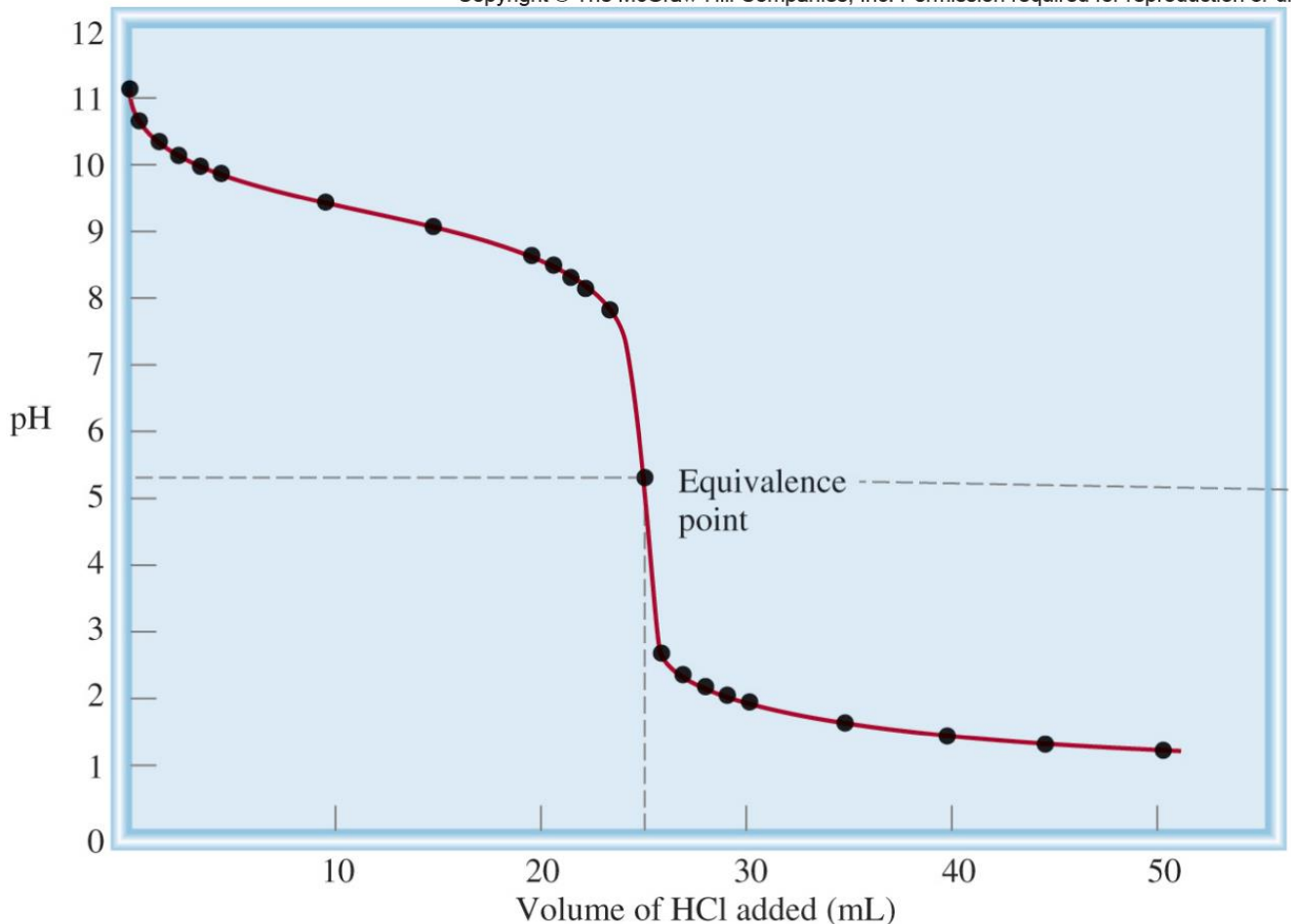


Answer the following questions on the next page:

1. Calculate the initial pH (K_a for acetic acid is 1.8×10^{-5}).
2. Why is $\text{pH} > 7$ at the equivalence point?
3. Calculate the pH at the equivalence point.
4. The pH rises slowly between 5 mL and 20 mL. Why?
5. Calculate the pH at 12.5 mL (half-way to the equivalence point).
6. After the equivalence point, the curve is identical to the strong acid/strong base titration. Why?

Titration of 25.00 mL of 0.100 M NH₃ with 0.100 M HCl (weak base, strong acid):

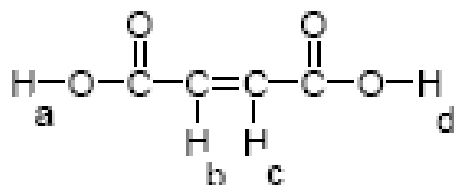
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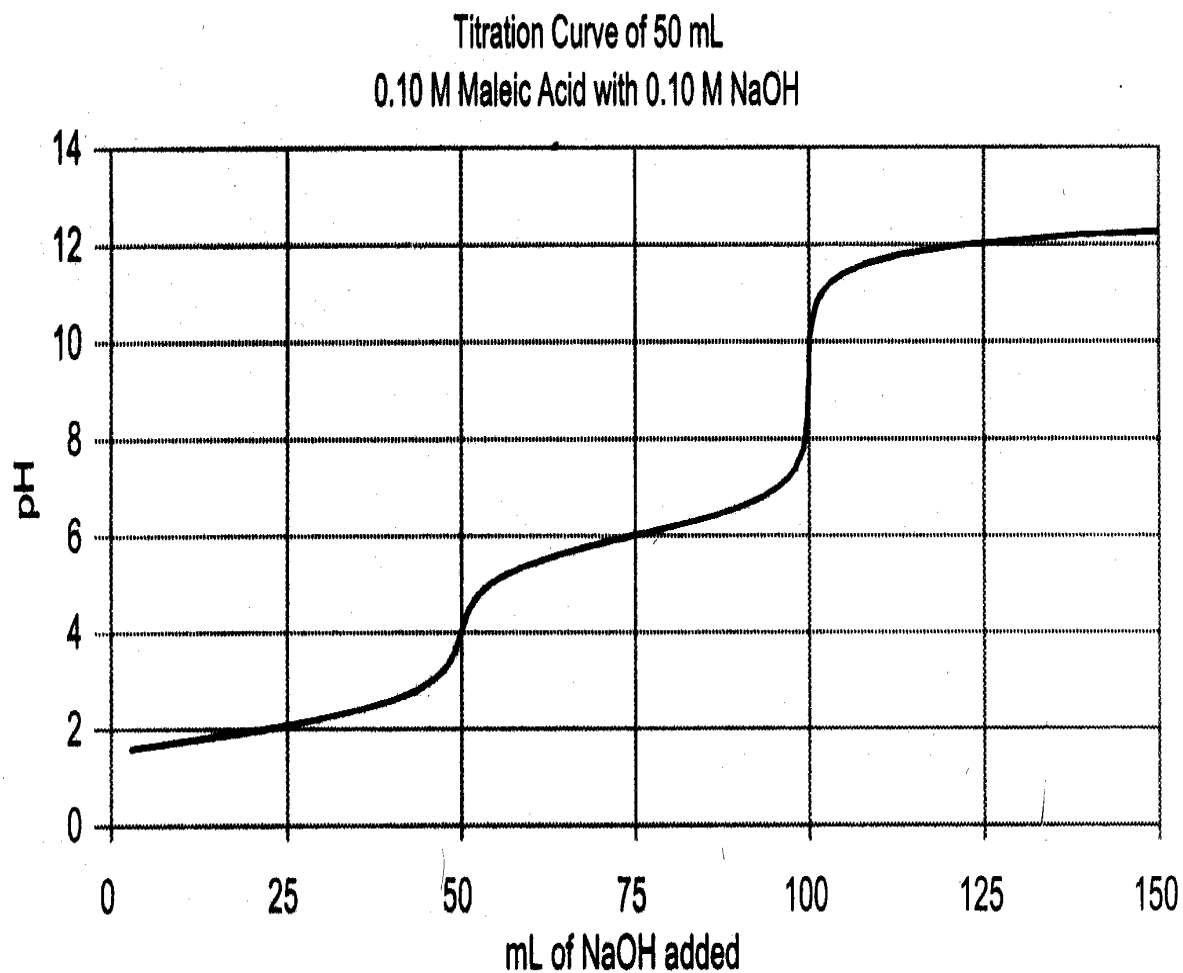
Answer the following questions on the next page:

1. Calculate the initial pH (K_b for ammonia is 1.8×10^{-5} ; It is coincidence the the K_b for ammonia is about the same as the K_a for acetic acid).
2. Why is $\text{pH} < 7$ at the equivalence point?
3. Calculate the pH at the equivalence point.
4. What is the pH half-way to the equivalence point?

Maleic acid is a diprotic acid (a dicarboxylic acid). Its formula is $C_4H_4O_4$. Its structure is shown below. Only hydrogens a and d ionize (do you understand why?)



For this titration, use the following symbols: H_2A , HA^- , A^{2-} , where $A = C_4H_2O_4$



What would the titration of a triprotic acid (such as phosphoric acid) look like?

↑ Acid strength increases	Acid strength	Conjugate acid	K_a	Conjugate base	K_b	Base strength
	Strong	HCl	∞	Cl^-	0	Negligible
		H_2SO_4	∞	HSO_4^-	0	
		HNO_3	~ 20	NO_3^-	$\sim 5 \times 10^{-16}$	
	Moderately strong	H_3O^+	1.0	<i>H_2O</i>	1.0×10^{-14}	Weak
	Weak	HSO_4^-	1.2×10^{-2}	SO_4^{2-}	8.3×10^{-13}	
		H_3PO_4	7.5×10^{-3}	<i>H_2PO_4^-</i>	1.3×10^{-12}	
		HF	7.2×10^{-4}	F^-	1.4×10^{-11}	
		CH_3COOH	1.8×10^{-5}	CH_3COO^-	5.5×10^{-10}	
		H_2CO_3	4.2×10^{-7}	<i>HCO_3^-</i>	2.4×10^{-8}	
<i>H_2PO_4^-</i>		6.2×10^{-8}	<i>HPO_4^{2-}</i>	1.6×10^{-7}		
NH_4^+		5.5×10^{-10}	NH_3	1.8×10^{-5}		
<i>HCO_3^-</i>		4.8×10^{-11}	CO_3^{2-}	2.1×10^{-4}		
<i>HPO_4^{2-}</i>	3.6×10^{-13}	PO_4^{3-}	2.7×10^{-2}			
Negligible	<i>H_2O</i>	1.0×10^{-14}	OH^-	1.0	Moderately strong	
	OH^-	0	O^{2-}	∞	Strong	
	H_2	0	H^-	∞		

Base strength increases
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