

Week 4 • Equilibrium

TEACHING IDEAS AND RESOURCES

Overview:

The challenge with equilibrium is that it has many faces. Luckily, there are some basic principles that we can establish and then you can examine the special cases and situations with your students. If you teach the basics carefully with your students, the later work will be easier. Here is how to approach **Week 4**.

- Read through these **Teaching Ideas** about this topic and the inevitable first question of the AP exam.
- Review the **Bluffer's Guides** for the areas of equilibrium. These are organized for my textbook, but I think the organization makes sense and will be applicable to most textbooks.
- Read the **Week 4 Labs and Demonstrations** handout that discusses ways to illustrate equilibrium ideas.
- Review the **various handouts** and **practice worksheets** that I use to teach this subject.
- Practice doing these problems. Ask questions and make comments in the **Discussion Board** about the Week 4 Resources and Week 4 AP Questions.

Grading:

These problems are always in the **calculator section** of the exam. Remember that if a student makes an error and loses a point on one part of a question and then uses that wrong information correctly, she/he can still get credit on subsequent parts of the question. Showing work is important.

Significant figures on final answers will also be checked. Answers will only lose credit (1 point maximum per problem) if the significant figures are off by **more than one**. Students may return to this problem after they have put away their calculators, so if a section of the question does not require calculations, the student may want to leave it until later if time is an issue.

Finally, students should remember that it is not necessary to earn all the possible points. Even for a "5" only 66% of the possible points are needed. Students should watch their time carefully and give themselves roughly **20 minutes** on this problem. Tell your students to bring a watch with them to the exam (not their cell phone) in case they are seated in a room without a clock or facing away from the clock. The proctors will not announce the time.

Basic Equilibrium Ideas:

Reactions Are Reversible:

Students are used to the idea that a reaction is a one-way situation. I introduce the idea that there are often reversible reactions when we look at liquid-vapor equilibria. In a closed system, for every molecule that evaporates, one condenses. We also build this idea into our model of weak acids.

Closed System:

Equilibrium ideas are used in various situations, but officially, for an equilibrium to be established, it must be a closed system (no products leave the system and no new reactants enter the system). The system is whatever we want to define it to be, however. A jar of water is a closed system. A solution in an open beaker is also a closed system for the solute in the solution (for non-volatile solutes and ignoring the solvent that evaporates over time).

Constant Macroscopic Properties:

Make the point that the properties of the system (color, pressure, temperature, concentrations, etc.) remain the same at equilibrium because the forward and reverse reactions are the same. Changes still occur, but no **net change** occurs.

Doesn't Matter Where You Begin:

You can reach the same equilibrium whether you begin with all reactants, all products, or any situation in between. An unlit candle is a good counter-example. It doesn't change, not because it is at equilibrium, but because there is a high activation energy that the reactants cannot supply at room temperature. If we began with $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$, we would not get to the same equilibrium point. This will be an important idea for some complex equilibrium problems in which you have some of each of the reactant and product particles. The trick is to "push" the equilibrium all the way one way or the other until one of the concentrations becomes zero and then let the system come to the same final equilibrium.

Driving Forces (Entropy and Enthalpy):

There are two driving forces for all reactions: a tendency toward minimum enthalpy (energy) and a tendency toward maximum entropy (randomness, disorder, spreadioutiness). Equilibrium results when these two driving forces drive a reaction in opposite directions. An especially clear example is the evaporation of water.



entropy drives the reaction toward the more disordered products \rightarrow

\leftarrow **enthalpy** drives the reaction toward the lower potential energy reactants

Equilibrium Constants:

The idea of the equilibrium constant is an easy first-year idea. Students need to be aware of why solids and liquids do not appear in the expression. They also need to be warned that they will see many different constants, K_a , K_b , K_h , K_c , K_p , K_{eq} , K_w , K_{sp} and should know the differences and the implied type of reactions for each. Students should know how to write K_c expressions and K_p expressions that are both K_{eq} expressions. They should be able to convert from one to the other. **Temperature** is the **only thing** that changes K_{eq} values. If the reaction is manipulated (reversed, doubled, etc.) corresponding changes in the K_{eq} occur. Also, when two reactions are combined, their K_{eq} 's can be combined. All of these ideas should be considered basic skills.

Le Châtelier's Principle:

A system at equilibrium is dynamic. Changing the system (putting a "stress" on the system) causes the system to shift toward the products or toward the reactants (or not at all). Students should understand these problems on two levels: **Applying** Le Châtelier's Principle and **explaining** the result using reaction rate. Le Châtelier's Principle gives the correct answer, but doesn't really get to the **reason why** the change occurs.

ICE Box:

A useful tool for stoichiometry in general and equilibrium problems in particular, is the I.C.E. box. Students fill the boxes using moles, molarity, or gas volumes, but definitely *not* grams.

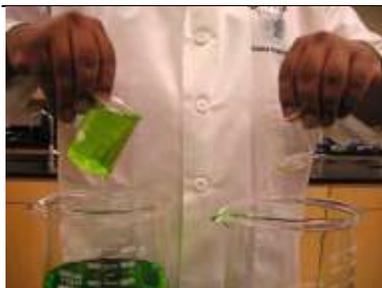
Example: If 1.00 mole $\text{N}_2(\text{g})$ and 4.00 moles $\text{H}_2(\text{g})$ are introduced into a 1.00-Liter container and allowed to come to equilibrium at a certain temperature, 1.80 moles of $\text{NH}_3(\text{g})$ is found at equilibrium. What are the equilibrium amounts of $\text{N}_2(\text{g})$ and $\text{H}_2(\text{g})$?

	$\text{N}_2(\text{g})$	+	$3 \text{H}_2(\text{g})$	\rightleftharpoons	$2 \text{NH}_3(\text{g})$
initial concentration	1.00 mol		4.00 mol		0 mol
change	-0.90 mol		-2.70 mol		+1.80 mol
equilibrium concentration	0.10 mol		1.30 mol		1.80 mol

The **initial** concentration row can be anything (watch for implied amounts, especially 0 M). Similarly, the **equilibrium** concentrations can be anything. The only row that **must** be in a stoichiometric ratio (1:3:2, in this case) is the **change** row.

The equilibrium constant could be calculated at this point. If the equilibrium constant is known, algebraic expressions can be used inside the boxes. This is where the fun begins.

Introducing Equilibrium:



Two Beaker Demo:

When I introduce equilibrium, I use an old demonstration. Two large beakers and two small beakers. I begin with all of the colored water in one beaker (the reactants). The two different-sized beakers represent the different tendencies for the forward and reverse reactions. The key idea is to ask students



“**When have I reached equilibrium?**” As I begin to scoop water out of the reactant beaker and into the product beaker, I also scoop water from the product beaker into the reactant beaker (at first it is just air, but I still go through the motions). Students begin to tell me we’ve reached equilibrium when the two levels are the same, but I keep scooping and other students say I’ve reached equilibrium when the water levels stop changing.

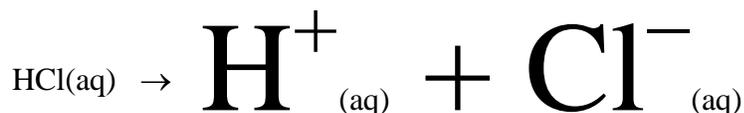
I ask another question, “**What is equal at equilibrium?**” Students soon realize that the water levels do not need to be the same for equilibrium, eventually we make the point that the **amount of water moved** forward and backwards is what really qualifies the situation as an equilibrium. We can test the idea by scooping both beakers of water in pouring them into handy graduated cylinders. Through all of this discussion, I keep scooping water forward and backward to make the point that once equilibrium is established, the observable properties (water level, in this case) do not change even though there **are** forward and reverse reactions occurring.



“**How can two different-sized beakers carry the same amount of water?**” is my last question. Students state that even though the beakers are different sizes, the water levels are also different. The beakers still carry the same amount of water. I make the point that the reaction rate depends on concentration as well as the inherent speed of the chemical change. Finally, I can stop moving the water back and forth. My arms are usually tired!

Two Early Examples:

When we first encounter **weak electrolytes**, I push for the model of reversible reactions to explain the fact that only some of the molecules are dissociated into ions. For example, vinegar, $\text{HC}_2\text{H}_3\text{O}_2(\text{aq})$, is a weak electrolyte while $\text{HCl}(\text{aq})$ is a strong electrolyte even when they are both at the same concentration. I say that HCl completely dissociates



while in acetic acid, only about 1% of the molecules dissociate. They all dissolve, but only 1% breaks into ions.



Why does the weak acid act in this fashion? Out of every 100 molecules, how does the one molecule “know” that **it** is the one that should break up? The answer is that the **strong acid**, HCl , only has a tendency to break up. The **weak acid**, $\text{HC}_2\text{H}_3\text{O}_2$, has a tendency to break up into ions, but has a **much stronger tendency** for the ions to stick together as a molecule.

I propose an analogy. I give 100 students each a flashlight and three dice, I tell them we want to represent a **strong acid**. Turn on the flashlight and roll the dice. If you roll three one's three times in row, turn your light off until the next roll. Essentially 100% of the flashlights should be on.

To represent a **weak acid**, I tell students to roll the dice. If they roll three one's or three two's (2 chances in 216) turn the light on until the next roll, otherwise keep the flashlight turned off. This would mean that on the average, about one person out of the 100 would have their flashlight on... and the flashlight that is on would change moment by moment.

I also point out the idea of opposing reactions when we encounter **liquid-vapor equilibrium** and **equilibrium vapor pressure**. The two opposing reactions involve a balance between the intermolecular forces of attraction between particles and the kinetic energy of the particles.

Equilibrium Calculations:

I think these are fun. You have the equilibrium equation, the ICE box, the equilibrium constant expression, and the equilibrium constant that are all related. You leave out one piece of information and utilize everything else to determine the missing information.

If students do not know how to do a problem, I suggest they do three things:

- write the equilibrium equation. Sometimes this is implied. For example, if a question states that the K_{sp} of $\text{Ca(OH)}_2 = 5.5 \times 10^{-6}$, the reaction is $\text{Ca(OH)}_2(\text{s}) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + 2 \text{OH}^{-}(\text{aq})$.
- draw your ICE box. Sometimes this is not necessary, but often it is a useful organizational tool and can get you started.
- write the equilibrium expression.

Being able to do something when you "don't know what to do" will have a calming effect. Often, students will see their way after they do these three steps.

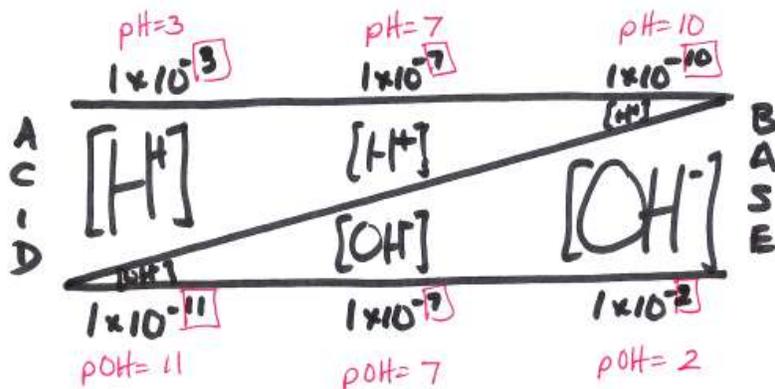
Approximations are often needed to solve problems unless students use the solve function on their graphing calculators to solve the quadratic equations that show up. If an approximation doesn't change the answer by more than 5%, it is valid. Students should check the validity of their approximations.

The reaction quotient, Q , is a useful idea. Substituting current concentrations into the equilibrium expression gives information about where the reaction is with respect to equilibrium. This idea shows up in K_{sp} calculations, the Nernst equation, and ΔG calculations.

Practice, practice, practice is the way to learn these calculations. Have students look for ideas to add to their "bag of tricks".

Water Equilibrium and pH:

I really like to use the "Z-diagram" to help students understand that every aqueous solution has some H^+ ions and OH^- ions in it. I begin with the autoionization of water, $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$, and apply Le Châtelier's Principle to simple acidic and basic solutions. As we add H^+ ions, the equilibrium shifts and the $[\text{OH}^-]$ decreases, etc. I also use in-between examples such as $[\text{H}^+] = 2.5 \times 10^{-5} \text{ M}$. We find the value of K_w of the water equilibrium. (Note that 1.0×10^{-14} is really only for 25°C .) We define pH as the "power of the $[\text{H}^+]$ " and mathematically use $\text{pH} = -\log[\text{H}^+]$.



I can refer back to this Z-diagram whenever I need to make a point about calculating pH, pOH, $[H^+]$, and $[OH^-]$. If you know any one of them, you really know all four.

Acid-Base Equilibria:

A weak acid is not a molecule that doesn't break up (dissociate) into ions, it is a molecule that has a tendency to break up but also a stronger tendency to go back together. It is represented by the acid dissociation equation:



Here, I use acetic acid as an example. The size represents the concentration of the species. If we want to, we can include $H_2O(l)$ in the equation. However, unless I am trying to make a point about Brønsted-Lowry acids and bases, I usually leave H_2O out for clarity.



We can write the K_{eq} expression for this equation. Since this is an acid, we call it the K_a . The smaller the K_a , the weaker the acid, that is, the less likely it is to dissociate into ions.

Weak bases, such as ammonia, $NH_3(aq)$ **require** $H_2O(l)$ to show how they increase the OH^- ion concentration.



I sometimes get myself confused with weak bases vs. **strong bases that do not dissolve**. Pretty much, NH_3 and similar molecules are the only weak bases we encounter. $Mg(OH)_2$ is not a weak base, it is a strong base that simply does not dissolve to much of an extent, however, the little that **does** dissolve **completely dissociates**. Contrast this with ammonia that **dissolves well**, but **doesn't dissociate** very much.

Polyprotic acids have one dissociation equation for each proton. H_2SO_4 is a strong acid, but only for the first proton. HSO_4^- would be considered a weak acid. $NaHSO_4$ and similar compounds are called **acid salts**. They are often used to standardize a base solution for a titration.

When calculating the pH of a diprotic acid solution, such as H_2S , only the first dissociation needs to be considered. That is, pretend H_2S is a monoprotic acid and K_{a1} is the K_a .

The theory behind strengths of acids depends on the type of acids. View the **online tutorial** here: <http://www.wwnorton.com/college/chemistry/gilbert2/chemtours.asp#16> called **Acid Strength and Molecular Structure**. Students should be able to compare strengths of HF, HCl, HBr and HI as well as HOCl, HClO₂, HClO₃ and HClO₄. Students should also be able to explain differences in H₃PO₄, H₂SO₄, and HClO₄. Size of the central atom, the number of oxygen atoms, and electronegativity of the central atoms are the critical factors.

Conjugate Acids and Bases & Hydrolysis:

The Brønsted-Lowry (B-L) definition of acids and bases is very useful. The focus on **transfer of protons** (H⁺ ions) broadens what we call an acid and a base over the Arrhenius definition. Students quickly pick up on the idea that H₂O(l) acts as a B-L base when we write: HC₂H₃O₂(aq) + H₂O ⇌ H₃O⁺(aq) + C₂H₃O₂⁻. It is important that they consider the reverse reaction and label H₃O⁺ as a B-L acid and C₂H₃O₂⁻ as a B-L base. Students are generally adept at picking out conjugate acid-base pairs.

When we look at the equation: NH₃(aq) + H₂O(l) ⇌ NH₄⁺(aq) + OH⁻(aq), we see that H₂O(l) now acts as an acid by donating a proton to NH₃. The important idea is that a molecule cannot always be labeled an acid or a base until you consider the molecule it reacts with. Water is **amphiprotic**; it can act as either an acid or a base. NH₃ is also amphiprotic. It can act as a donor and become NH₂⁻ or as an acceptor and become NH₄⁺.

If we generalize, we can see that if a molecule has an H atom, it can act as a B-L acid. CH₄ can donate (not well, but it CAN) to become CH₃⁻ (methoxide, which is a very strong B-L base). Any molecule with a lone pair of electrons can act as a proton acceptor, a B-L base. Acetic acid can do this to become CH₃C(OH)₂⁺. It is not a good base, but it has its uses in determining which strong acid is the strongest.

Let's look back at the dissociation equation for acetic acid:



It is useful to know that the equilibrium **favors the side with the weaker acid and weaker base**. Think about this for a moment. The two acids in the above equation are HC₂H₃O₂ and H₃O⁺. H₃O⁺ is the stronger acid. If HC₂H₃O₂ were the **better proton donor** (stronger acid), we wouldn't see a lot of **it**, we'd see it **after** it had donated its proton as C₂H₃O₂⁻. We can think about the two bases in a similar fashion. There are always questions asking you to pick out the stronger acid or stronger base.

The really useful concept in all this is the fact that C₂H₃O₂⁻ is a base; it is a proton acceptor. The equation that shows this is: C₂H₃O₂⁻ + H₂O(l) ⇌ HC₂H₃O₂(aq) + OH⁻(aq). We call this hydrolysis (water breaking) because the base, acetate ion, is a proton acceptor and accepts a proton right off of the water molecule. This increases the hydroxide ion concentration making the solution basic. Written to scale, the equation is:



You can write the K_{eq} for this equation. Since acetate ion is a base, this is the K_b. The K_b for a **conjugate base** can be calculated from the K_a of the weak acid because K_a · K_b = K_w or K_b = $\frac{K_w}{K_a}$. Students can prove this to themselves by writing out the expressions for K_a and K_b and canceling common terms. This only works for conjugate acid-base pairs, however.

The pH of a buffer when $[HA] = [A^-]$ is easy. If the ratio is not 1:1, the pH will be a little higher (more basic) if the conjugate base is more concentrated than the acid. Conversely, if the acid concentration is greater than the conjugate base concentration, the pH of the solution will be a little lower (more acidic). This situation is dealt with quantitatively with the **Henderson-Hasselbach** equations shown here as they appear on the AP exam.

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

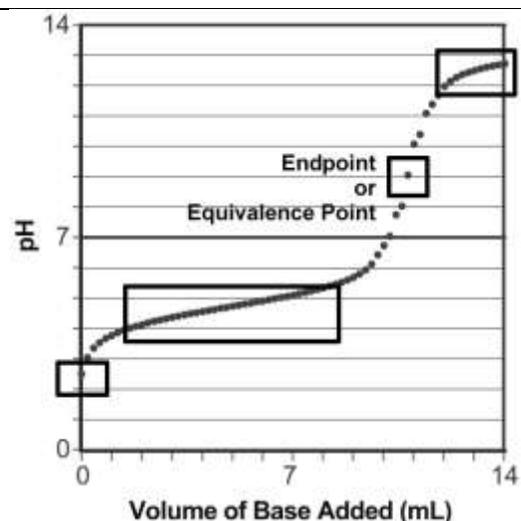
$$pOH = pK_b + \log \frac{[HB^+]}{[B]}$$

A **half-titration** is a laboratory method to find the K_a of an unknown acid. Take any sample of an unknown acid, split it into **two equal portions**, add NaOH to neutralize **one** of the portions (using phenolphthalein as an indicator) and then pour the two halves back together. You have created a buffer and the pH of the buffer is the pK_a of the unknown acid.

Titrations and Titration Curves:

A titration curve is simply a **graph of the pH** as base is added to an acid or acid is added to base. The graph looks different depending on whether you are neutralizing a strong acid or a weak acid. Neutralizing a weak base with strong acid results in an inverted titration curve. Diprotic acids have a different shape as well.

Students need to be able to find the **equivalence point** on these graphs. Notice that when you **neutralize** the acid, you don't end up with a **neutral** solution (because of the conjugate base formed). This overlap of terminology confuses everyone. Each region on the curve represents a different situation and a different calculation. It can all be a little overwhelming, but if broken down into separate situations, can be mastered.



I have two entire **separate handouts** about titration curves and the calculations involved as well as a practice worksheet. My students find this one of the toughest ideas in the AP course. Several very useful **online tutorials** exist here: <http://www.wwnorton.com/college/chemistry/gilbert2/chemtours.asp#16> Look for the two tutorials about **titrations**.

Solubility Equilibria:

When you get to this chapter, it is often a good time to review and re-test the solubility rules. Compounds we memorized with low solubility are what this chapter is all about. We commonly say that solids such as $AgCl(s)$ are insoluble, but in reality, everything dissolves a little.

The equation would be $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$. The equilibrium constant is called the “solubility product” constant, K_{sp} . Since the reactant is always a solid, the expression has no denominator. $K_{sp} = [Ag^+][Cl^-]$. A **saturated solution** is the equilibrium state for these problems.

The reverse of this reaction is the net equation for a **precipitation** reaction. The K_{sp} can be used to identify **whether a precipitate will form** when two dilute solutions are mixed. Determine the concentrations of the ions (be careful to take into account any **dilution** that occurs by mixing two solutions together). Substitute the ion concentrations into the K_{sp} expression. The result is the Q_{sp} . If $Q_{sp} > K_{sp}$, then too many ions are in solution and a precipitate will form. If $Q_{sp} < K_{sp}$, then the solution is unsaturated. In a saturated solution, $Q_{sp} = K_{sp}$. I've heard the Q_{sp} called simply Q and also T.I.P., the “trial ion product.”

A common question with these equilibria is determining the **solubility** of the solid given its K_{sp} or vice versa.. If we define solubility, s , as the molarity of the most concentrated solution you can make, then the problem can be made into an ICE box problem. I use the variable in the solid column even though it is not really part of the equilibrium.

	$\text{AgCl}(s)$	\rightleftharpoons	$\text{Ag}^+(aq)$	+	$\text{Cl}^-(aq)$
initial concentration	s		$0 \underline{M}$		$0 \underline{M}$
change	$-s$		$+s$		$+s$
equilibrium concentration	0		s		s

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (s)(s) = s^2$$

However, for a 2:1 compound like PbCl_2 , the problem changes a little:

	$\text{PbCl}_2(s)$	\rightleftharpoons	$\text{Pb}^{2+}(aq)$	+	$2 \text{Cl}^-(aq)$
initial concentration	s		$0 \underline{M}$		$0 \underline{M}$
change	$-s$		$+s$		$+2s$
equilibrium concentration	0		s		$2s$

$$K_{sp} = [\text{Pb}^{2+}] [\text{Cl}^-]^2 = (s)(2s)^2 = 4s^3$$

for Cl^- ion, the value is **doubled** and **squared**.

In a 1:3 compound one value will be **tripled** and **cubed**. Summarizing:

Ion Ratio:	1:1	1:2 or 2:1	1:3 or 3:1	2:3 or 3:2
Example:	AgCl	PbCl_2	Ag_3PO_4	Bi_2S_3
$K_{sp} =$	s^2	$4s^3$	$27s^4$	$108s^5$

Solubility is also listed in units of g/100 mL. Conversion to or from molarity would be needed.

If the question asks about the solubility of AgCl in a solution of NaCl , the **common ion effect** comes into play. Students often try to make up an equation such as $\text{AgCl}(s) + \text{NaCl}(aq) \rightleftharpoons \text{Ag}^+(aq) + \text{Na}^+(aq) + 2\text{Cl}^-(aq)$. They need to remember that the equilibrium remains, $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+(aq) + \text{Cl}^-(aq)$ and **we are interested in how the new chemical, $\text{NaCl}(aq)$, affects that equilibrium**. In this case, the ICE box is identical to the ICE box at the top of this page except that **there is now an initial concentration of $\text{Cl}^-(aq)$** . NaCl and AgCl have Cl^- in common... the common ion effect. Using a Le Châtelier's Principle argument, students can see that the concentration of Ag^+ will be less, that is, less $\text{AgCl}(s)$ will dissolve. We have increased the chances that a silver ion will collide with a chloride ion to make silver chloride solid and have reduced the solubility.

Finally, some solids are **sensitive to the pH** of the dissolving solution. If the anion in a solid is the **conjugate base of a weak acid**, adding H^+ to the solution will allow the anion to form the weak acid and make it unavailable for the equilibrium. Le Châtelier's Principle shows that the solid will dissolve better. If we raise the pH, the solubility will decrease.

For example:



if we add H^+ , H_2S forms and reduces $[\text{S}^{2-}]$:

More $\text{Ag}_2\text{S}(s)$ dissolves so the solubility increases. This pH dependency is true of compounds with anions such as carbonate, fluoride, sulfide, sulfite, phosphate, etc., not compounds with nitrate, chloride, bromide, iodide, etc.