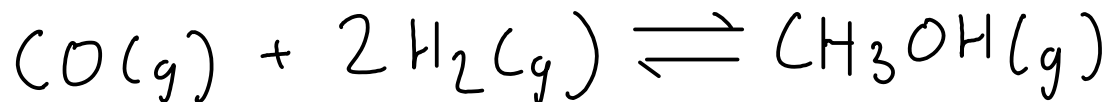


- Pressure can affect a GAS-PHASE equilibrium ... sometimes. How?

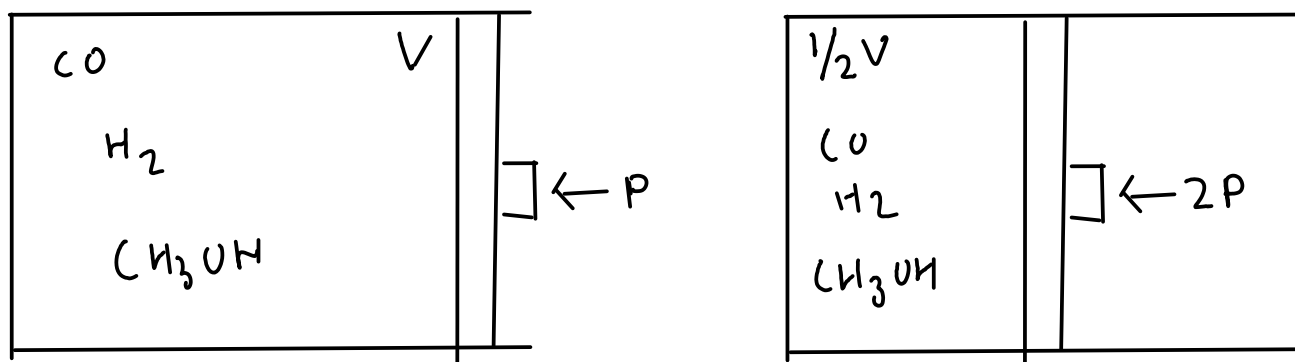


... how might pressure affect this equilibrium?

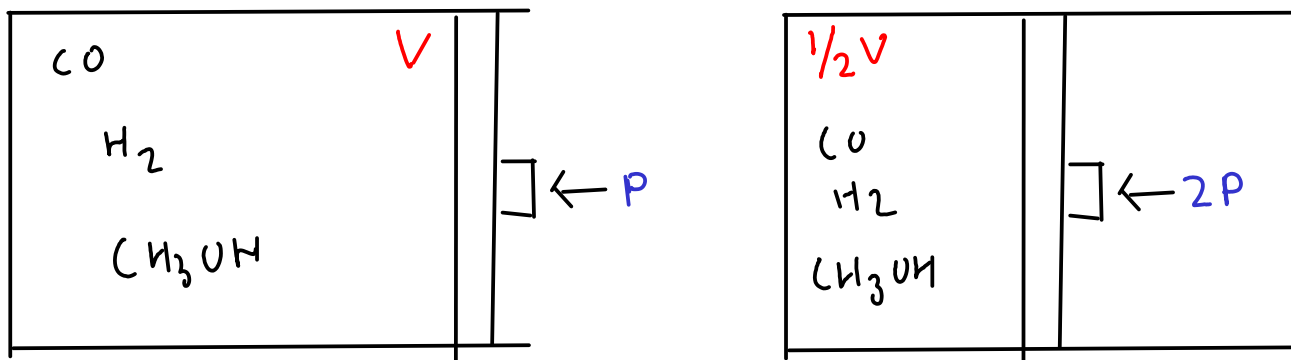
- If the change in pressure CHANGES CONCENTRATIONS, then this equilibrium would be disturbed and Le Chateleur's Principle would apply.

- Adding an INERT GAS would change pressure, but would it change concentration of the gases? NO - so addition of argon would have no effect on the equilibrium!

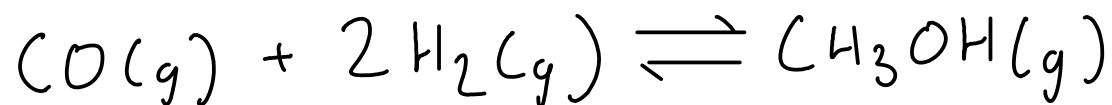
- What about COMPRESSION?



... compression increases pressure by DECREASING total volume.



... but this volume change affects ALL concentrations the same way. In this example, each concentration is DOUBLED.



$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{(1)}{(1)(1)^2} = 1$$

For simplicity,  
let's assume  
 $K_c = 1$ , and all  
concs = 1M

Doubling  
concentrations  
gives  $Q =$

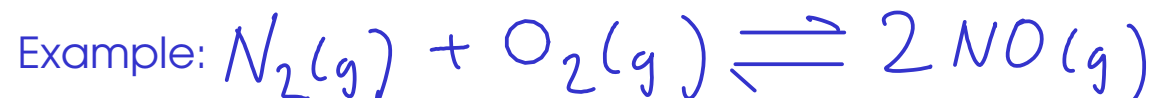
$$\frac{2}{(2)(2)^2} = \frac{1}{4}$$

$Q < K_c$ , so equilibrium shifts to the RIGHT, forming more methanol at the expense of hydrogen and carbon monoxide.

In general, compressing an equilibrium reaction in the gas phase will cause the equilibrium to shift towards the side with fewer moles of gas. This causes the pressure to decrease.

In general, decompressing an equilibrium reaction in the gas phase will cause the equilibrium to shift towards the side with more moles of gas. This causes the pressure to increase.

HOWEVER, this can only be true IF there's a side of the reaction with more moles of gas than the other. If both sides of the reaction have the SAME number of moles of gas, then a pressure change will NOT affect the equilibrium.



... would not respond to a pressure change.

## <sup>119</sup> FACTORS THAT MAY AFFECT EQUILIBRIUM

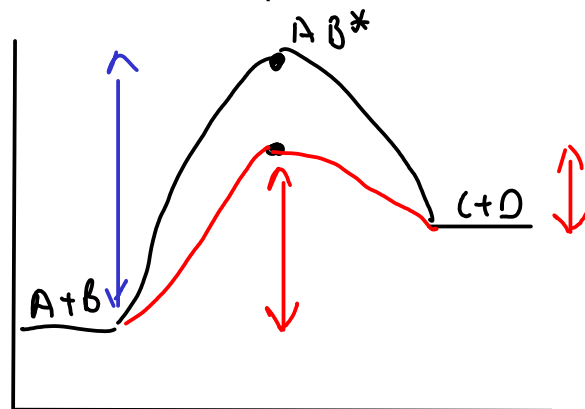
① TEMPERATURE (effect depends on whether reaction is endothermic or exothermic)

- Changes rate of reaction, too!
- ... changes  $K_c$

② PRESSURE - only for gas-phase reactions which have different numbers of moles of gas on each side of the equilibrium. Otherwise, no effect.

- ... no change of  $K_c$

③ CATALYSTS - do NOT affect equilibrium, but make the equilibrium state occur more quickly.



The catalyst raises BOTH forward and reverse rates, so it doesn't affect the composition of the equilibrium mixture!

④ CONCENTRATION - Le Chateleur's Principle applies for changing concentrations. An equilibrium will shift to counteract a change in concentration of reactant or product.

- ... doesn't change  $K_c$ .

## ACID/BASE EQUILIBRIUM

- Several scientific theories exist that define acid-base chemistry. We will discuss THREE of these theories.
- These theories differ in the way that acids, bases, and their associated reactions are defined.
- Typically, the newer theories include MORE chemicals under the umbrella of "acid-base chemistry"!

### THREE ACID-BASE THEORIES

- ① Arrhenius theory
- ② Bronsted-Lowry theory
- ③ Lewis theory

## ARRHENIUS THEORY

- The oldest model of acid-base chemistry!

- Only applicable to systems where WATER is the solvent!

ACIDS are substances that ionize in water to increase the concentration of HYDRONIUM ION



Hydronium ion

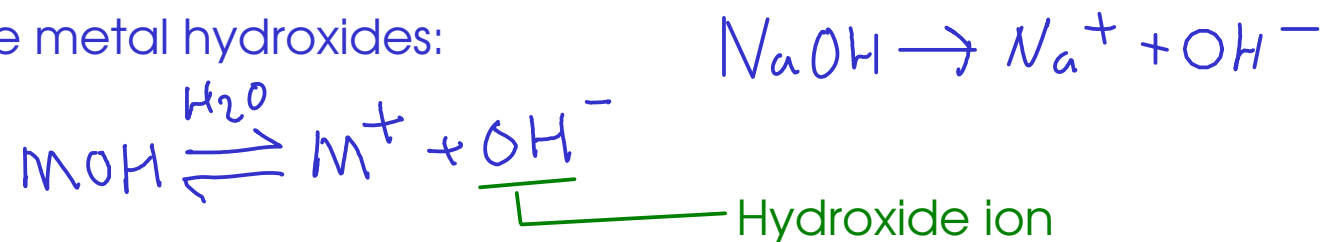


"Hydrogen ion" - doesn't really exist as a free ion in water, but a convenient simplification!

## ARRHENIUS THEORY

BASES are substances that ionize in water to increase the concentration of HYDROXIDE ION

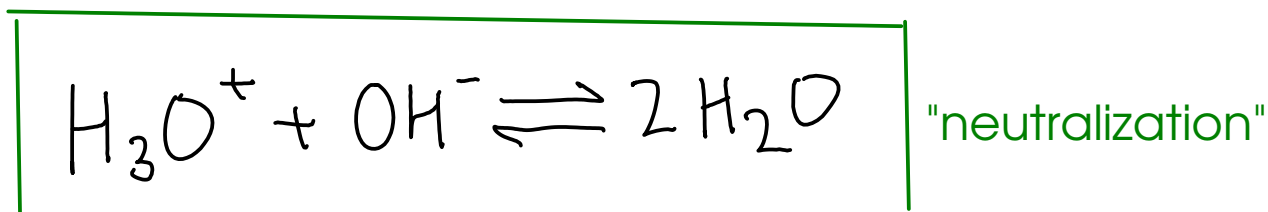
For soluble metal hydroxides:



For other Arrhenius bases:



An Arrhenius acid base reaction can be represented by:



or, using hydrogen ion instead of hydronium



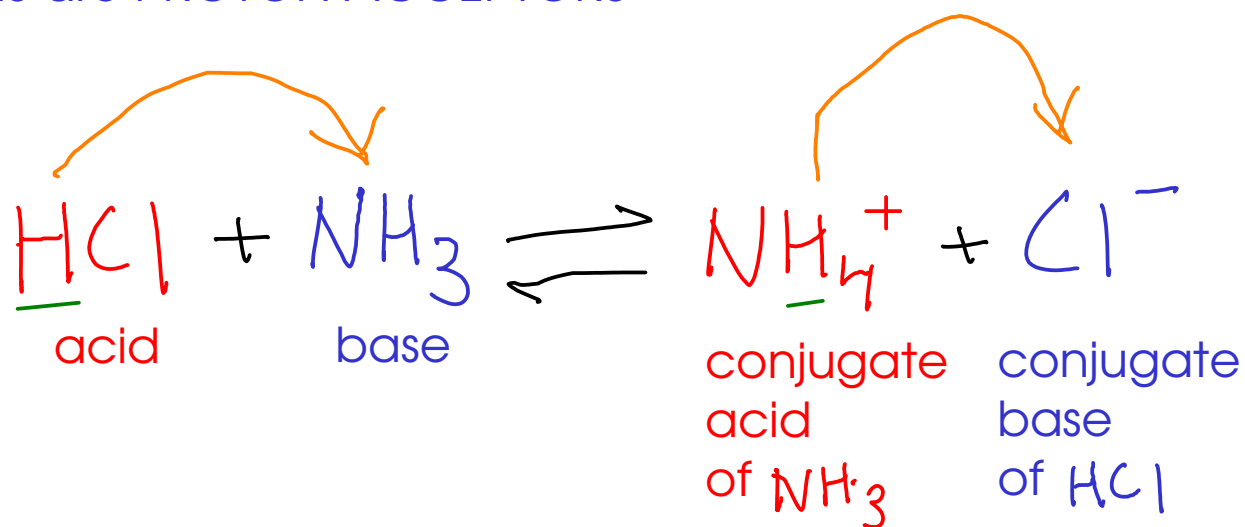
## BRONSTED-LOWRY THEORY

- Bronsted-Lowry theory views acid-base reactions as PROTON TRANSFER reactions!

$H^+$  ions!

ACIDS are PROTON DONORS

BASES are PROTON ACCEPTORS



A CONJUGATE PAIR is an acid and a base that differ by a proton!



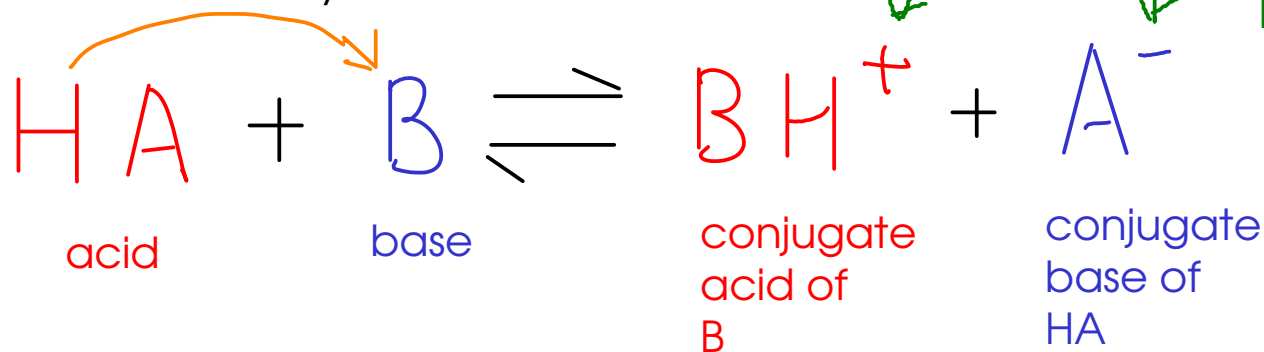
... a few examples of conjugate pairs:

Species	Conjugate
$\text{NH}_3$	$\text{NH}_4^+$
$\text{H}_2\text{O}$	$\text{OH}^-$
$\text{H}_2\text{O}$	$\text{H}_3\text{O}^+$
$\text{HC}_2\text{H}_3\text{O}_2$	$\text{C}_2\text{H}_3\text{O}_2^-$

RED for acid

BLUE for base

A generic Bronsted-Lowrey acid-base reaction:

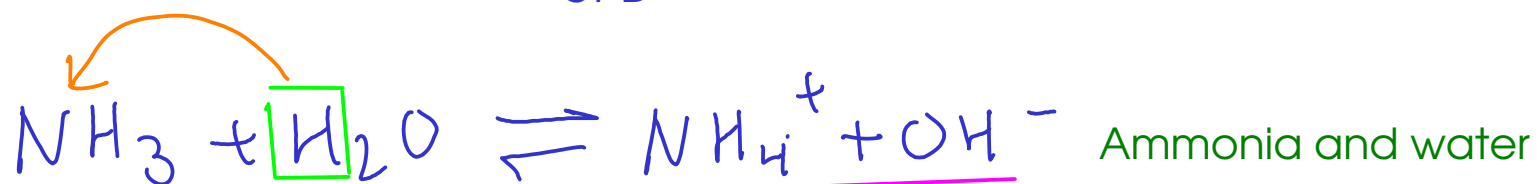
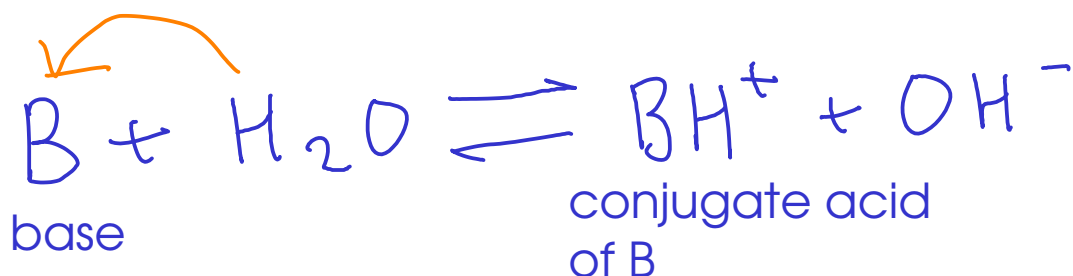
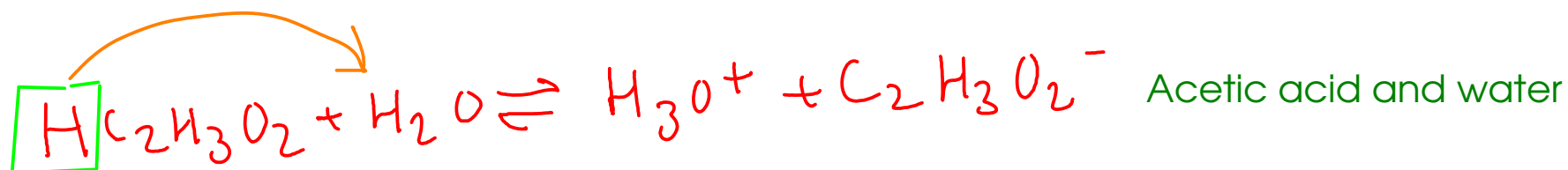
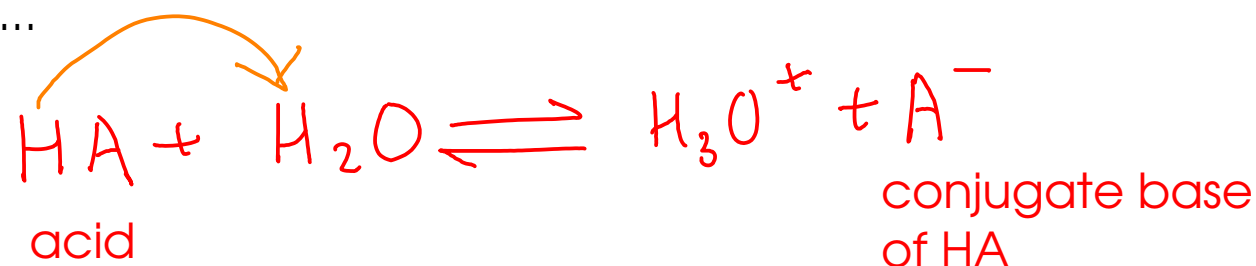


These charges are RELATIVE to whatever charge B and HA originally had...

... you should be able to write the products of a Bronsted-Lowry acid-base reaction, identifying the CONJUGATE PAIRS

# BRONSTED-LOWRY THEORY

IN WATER...



This is why we often call an ammonia/water solution "ammonium hydroxide"!

In the red reactions, water functions as a base. In the blue reactions, water functions as an acid!

## LEWIS THEORY

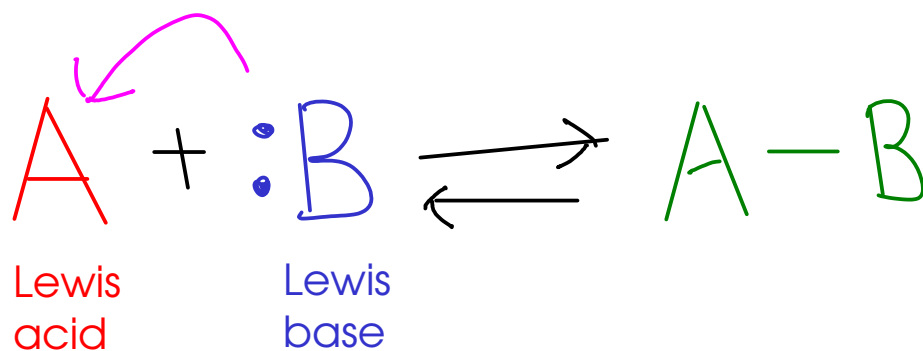
- Lewis theory treats acid-base chemistry as ELECTRON-TRANSFER chemistry involving pairs of electrons
- Lewis acid-base reactions form new covalent bonds (of interest to organic chemists!)

ACIDS are ACCEPTORS of electron pairs

... this is why some METAL IONS, even though they contain no hydrogen ions, can exhibit ACIDIC character. Many metal ions can accept a pair of electrons to form a COMPLEX with a Lewis base! ex:  $Ag(NH_3)_2^+$

BASES are DONORS of electron pairs.

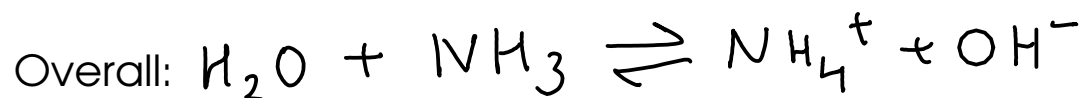
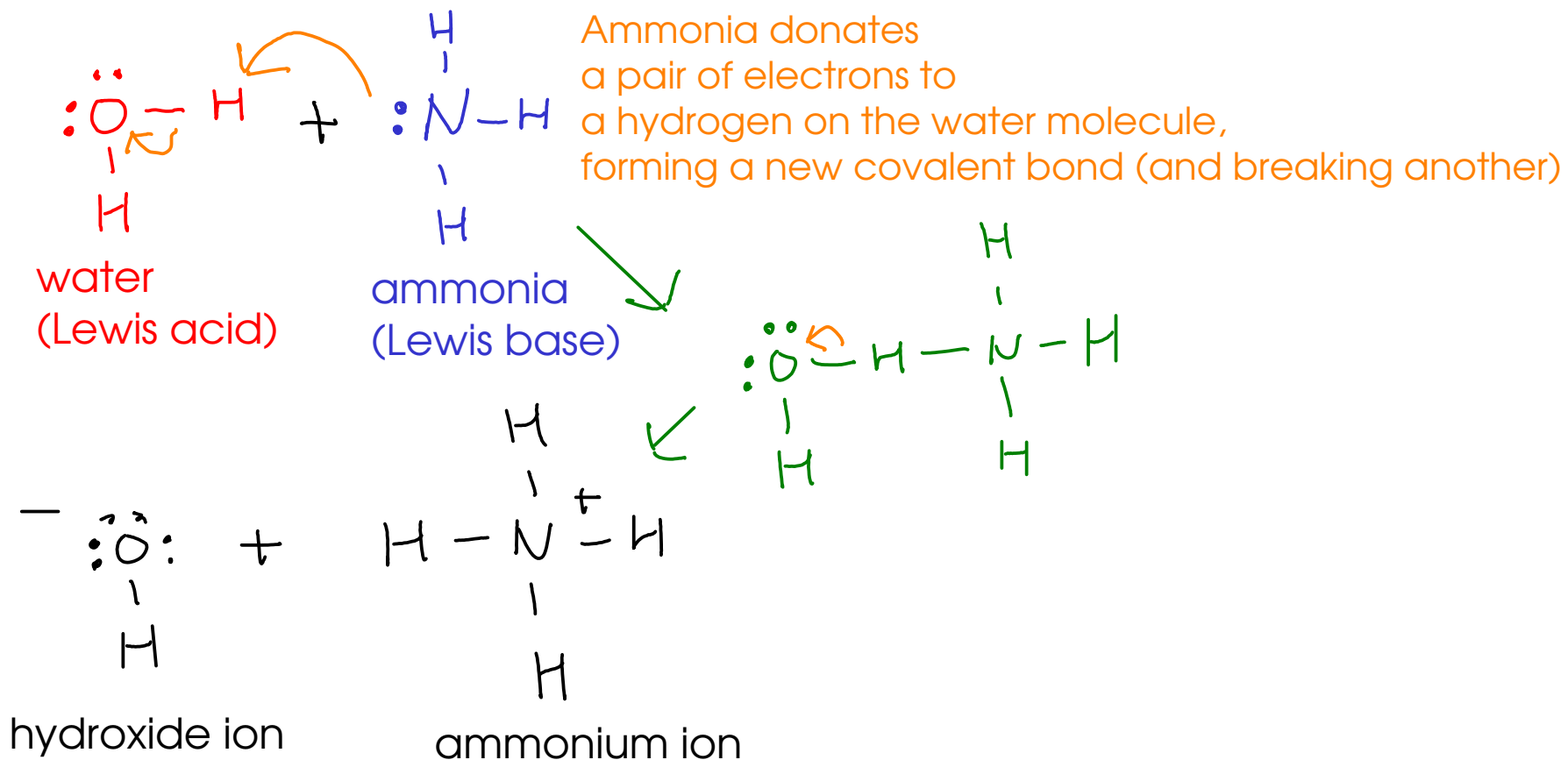
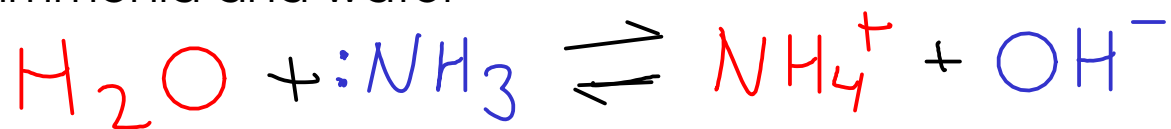
... so, Lewis bases have LONE PAIRS OF ELECTRONS in their Lewis structures



... In a Lewis acid-base reaction, electrons are donated from the Lewis base to the Lewis acid. This forms a new COVALENT BOND between the acid and the base.

LEWIS THEORY

Example: ammonia and water



## <sup>128</sup> COMPARING THE THEORIES

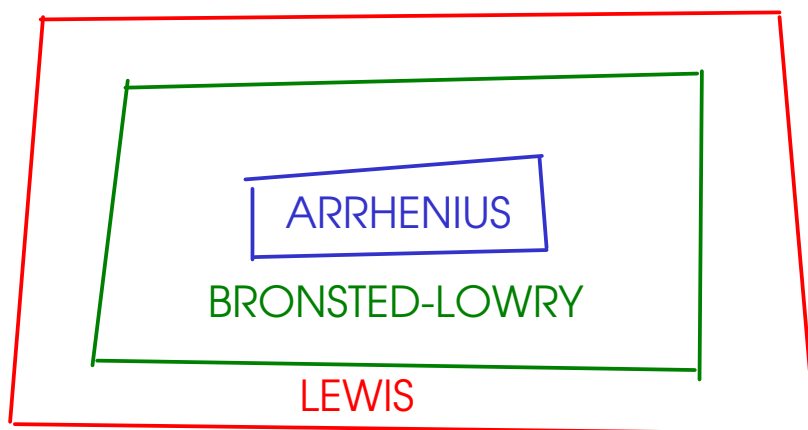
- From Arrhenius to Lewis, the definitions get broader as you go along. In other words, the later definitions include MORE SUBSTANCES under the acid/base umbrella.

If something is an Arrhenius acid, it is also an acid in the Bronsted or Lewis picture.

If something is an Arrhenius base, it is also a base in the Bronsted or Lewis picture.

All Bronsted acids are Lewis acids, and all Bronsted bases are Lewis bases.

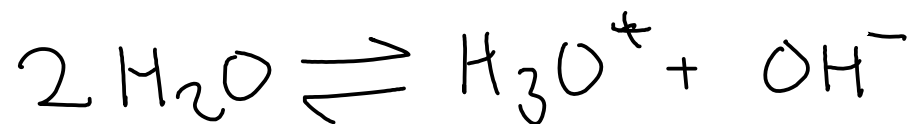
... but not all Lewis acids/bases (like the metal ions) are Bronsted or Arrhenius acids/bases.



... We will primarily use the BRONSTED-LOWRY theory from this point in the course!

## WATER CHEMISTRY

- Water self-ionizes!



or



This is an equilibrium reaction!

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

(X) = molar concentration of "X"

In aqueous solution, ( $\text{H}_2\text{O}$ ) is essentially constant, so we roll that into K.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

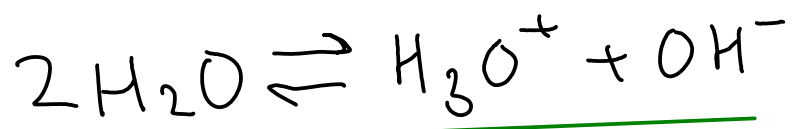
This is the value at 25C

## WATER CHEMISTRY

- The self-ionization of water has a small equilibrium constant. What does this imply?

THE CONCENTRATION OF HYDROXIDE AND HYDRONIUM ION IN PURE WATER IS VERY SMALL!

How small?



In pure water, the concentration of hydroxide and hydronium must be equal, since they are formed at the same time and at the same ratio from the ionization reaction of water.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1 \times 10^{-14}$$

Solve...

Let 'x' equal the change in concentration of hydronium ion...

$$(x)(x) = 1.0 \times 10^{-14}$$

$$x = 1.0 \times 10^{-7} \text{ M} = [\text{H}_3\text{O}^+] = [\text{OH}^-]$$

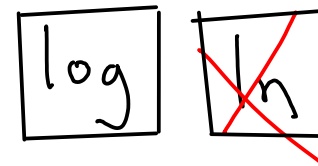
## "p" NOTATION

- "p" notation helps us deal with the very small numbers we encounter when working with acids, bases, and water.

- based on log base 10

"p" means  $-\log_{10}$

On a calculator, use



So,

$$\text{pH} = -\log_{10} [\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

$$\text{pOH} = -\log_{10} [\text{OH}^-]$$

$$[\text{OH}^-] = 10^{-\text{pOH}}$$



"p" NOTATION

- Apply "p" notation to the water self-ionization reaction!

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

becomes ...

$$pK_w = \text{pH} + \text{pOH} = 14.00$$

Taking the "p" (negative log base ten) of the equilibrium constant is often used for BUFFER SOLUTIONS, which we'll discuss later!

## ACIDITY AND ALKALINITY

- At  $\text{pH} = 7$ ,  $\text{pH} = \text{pOH}$ . The solution is considered NEUTRAL

Also,  $[\text{H}^+] = [\text{OH}^-]$ !

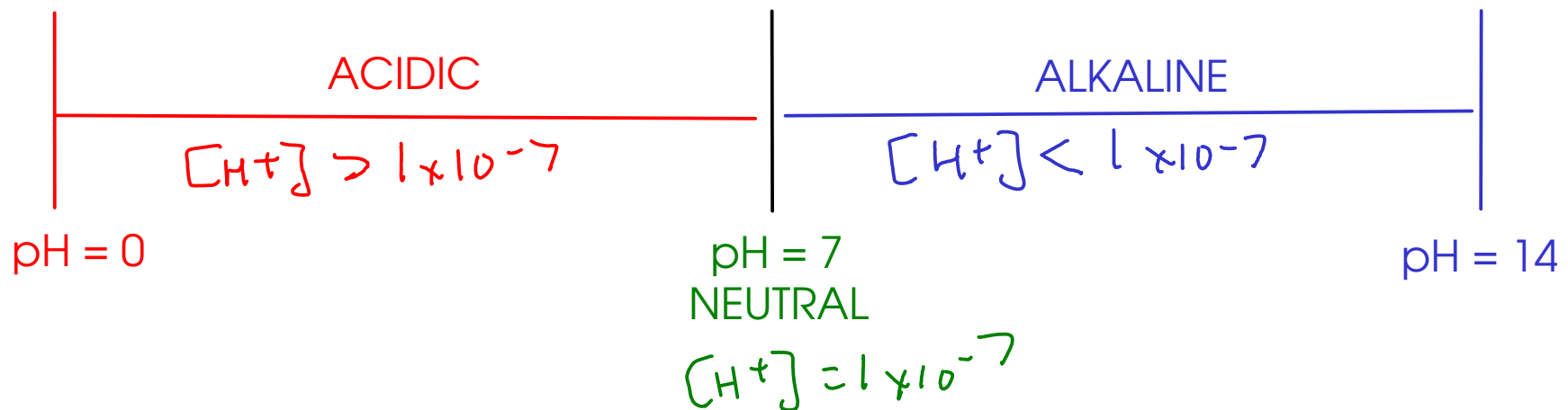
- At  $\text{pH} < 7$ ,  $\text{pH} < \text{pOH}$ . The solution is considered ACIDIC

Also,  $[\text{H}^+] > [\text{OH}^-]$ !

- At  $\text{pH} > 7$ ,  $\text{pH} > \text{pOH}$ . The solution is considered ALKALINE (BASIC)

Also,  $[\text{H}^+] < [\text{OH}^-]$ !

The pH scale...



## pH AND TEMPERATURE

$$pK_w = pH + pOH = 14.00$$

This equation is valid at room temperature, specifically 25°C.

Equilibrium constants depend on TEMPERATURE, and change with temperature.

So, the "neutral" pH (where the concentration of hydroxide and hydronium ions are equal) CHANGES with changing temperatures

This change is important at temperatures greatly different from 25°C.

As an example, consider average "normal" human body temperature: 37°C

$$\text{At } 37^\circ\text{C}, \quad pK_w = 13.60$$
$$pH \text{ of neutral solution} = \underline{\underline{6.8}}$$