$$\frac{x}{(0.100-x)^2} = 49$$

$$x = 49(0.100-x)^2$$

$$\downarrow \quad (a-b)^2 = a^2-2ab+b^2$$

This is a second order equation in "x", which means we can use the quadratic equation. We just need to rearrange it to get the quadratic form.

The QUADRATIC EQUATION:

$$ax^2+bx+c=0$$

$$x = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$$

Each quadratic has two solutions (see the +/- part of the equation), but only one of them will be the correct chemical solution.

$$x = 49(0.0100 - 0.200x + x^2)$$

$$x = 0.49 - 9.8x + 49x^2$$

$$0 = 49x^2 - 10.8x + 0.49$$

$a = 49 \quad b = -10.8 \quad c = 0.49$

$$x = \frac{+10.8 \pm \sqrt{(-10.8)^2 - 4(49)(0.49)}}{2(49)} = \frac{10.8 \pm \sqrt{20.6}}{98}$$

$x = 0.157$ or $x = 0.0634$

The quadratic gives two solutions, but only one of them actually works for the CHEMICAL problem. How do we know which is the right one?

Species	[Initial]	Δ	[Equilibrium]
PCl_5	0	+X	X
PCl_3	$\frac{0.400\ mol}{4.00\ L} = 0.100$	−X	0.100 − X
Cl_2	$\frac{0.400\ mol}{4.00\ L} = 0.100$	−X	0.100 − X

x = ~~0.157~~ or x = 0.0639

↳ The answer of x=0.157 gives us NEGATIVE concentrations for the chlorone gas and phosphorus trichloride, which is impossible. The correct x is 0.0639

FInd concentrations by plugging "x" into the chart.

PCl_5 : x : 0.064 M PCl_5

PCl_3 : .100 − x : 0.036 M PCl_3

Cl_2 : .100 − x : 0.036 M Cl_2

Kc = 49, which says that we should have more products in the mixture than reactants. That agrees with our answer!

An 8.00 L reaction vessel at 3900C is charged with 0.850 mol of nitrogen and oxygen gases. Find the concentration of all species at equilibrium.

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \quad K_c = 0.0123$$

$$\boxed{K_c = \frac{[NO]^2}{[N_2][O_2]} = 0.0123}$$

Make a chart so that we can express all these concentrations in terms of one variable.

Species	[Initial]	Δ	[Equilibrium]
N_2	$\frac{0.850\text{ mol}}{8.00\text{ L}} = 0.10625$	$-x$	$0.10625 - x$
O_2	$\frac{0.850\text{ mol}}{8.00\text{ L}} = 0.10625$	$-x$	$0.10625 - x$
NO	0	$+2x$	$2x$

Let "x" equal the change in nitrogen gas concentration

$$\frac{(2x)^2}{(0.10625-x)(0.10625-x)} = 0.0123$$

$$\frac{(2x)^2}{(0.10625-x)^2} = 0.0123$$

This can be solved via the quadratic equation, but there's another way!

$$\sqrt{\frac{(2x)^2}{(0.10625-x)^2}} = \sqrt{0.0123}$$

Since the left side is a squared term and the right side is just a number, we can take the sqare root of both sides!

$$\frac{2x}{0.10625-x} = 0.1109053651$$

$$2x = (0.1109053651)(0.10625-x)$$

$$18.03339269x = 0.10625-x$$

$$19.03339269x = 0.10625$$

$$x = 0.0055822943$$

Species	[Equilibrium]
N_2	$0.10625-x$
O_2	$0.10625-x$
NO	$2x$

Plug value for "x" back into the chart to find concentrations.

$$\begin{aligned} N_2 &: .10625-x = \boxed{0.101\ m\ N_2} \\ O_2 &: .10625-x = \boxed{0.101\ m\ O_2} \\ NO &: 2x = \boxed{0.0112\ m\ NO} \end{aligned}$$

This equilibrium constant is small (Kc=0.0123), so we expect the final mixture to be mostly products ... which is what we calculated!

PRESSURE AND EQUILIBRIUM

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

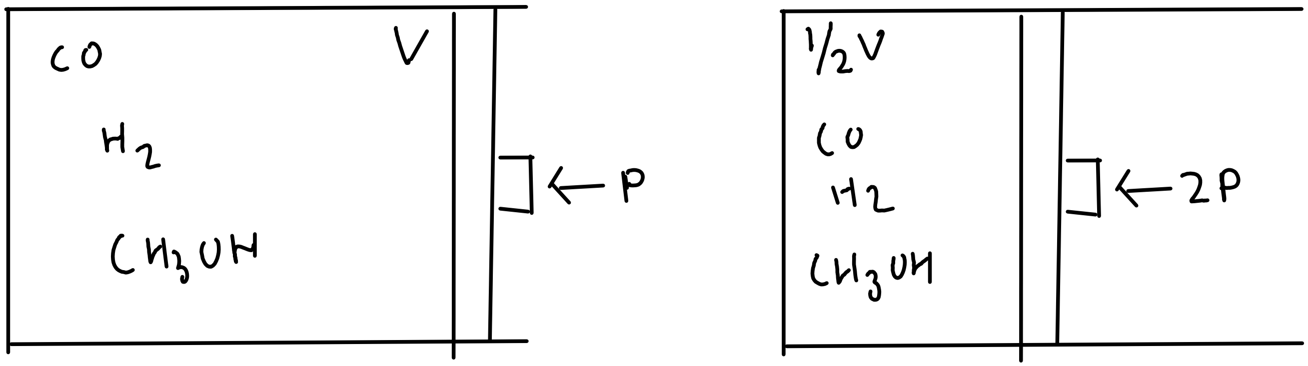
$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

... how might pressure affect this equilibrium?

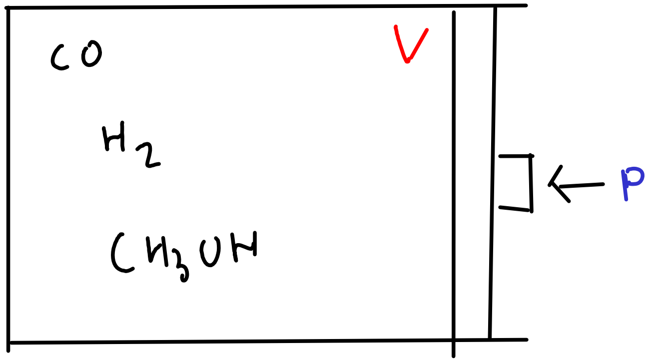
- If the change in pressure CHANGES CONCENTRATIONS, then this equilibrium would be disturbed and Le Chateleir's Principle would apply.

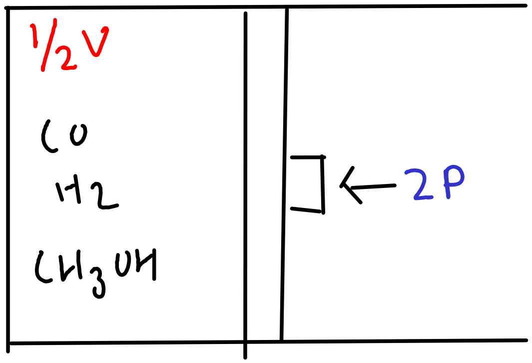
  - Adding an INERT GAS would change pressure, but would it change concentration of the gases? NO - so addition of argon would have no effect on the equilibrium!

  - 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.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} \qquad \frac{(1)}{(1)(1)^2} = 1$$

For simplicity, let's assume Kc = 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.

Example: $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

... would not respond to a pressure change.

FACTORS THAT MAY AFFECT EQUILBRIUM

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

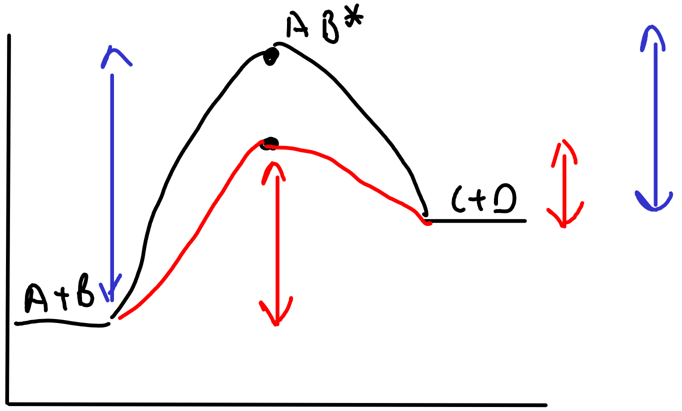
- Changes rate of reaction, too!

... changes Kc

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

... no change of Kc

③ CATALYSTS - do NOT affect equilibrium, but make the equilbrium 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 Chateleir's Principle applies for changing concentrations. An equilibrium will shift to counteract a change in concentration of reactant or product.

... doesn't change Kc.

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

$$HA + H_2O \rightleftharpoons \underbrace{H_3O^+}_{} + A^-$$

Hydronium ion

or, for simplicity: $HA \overset{H_2O}{\rightleftharpoons} \underbrace{H^+}_{} + A^-$

"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:

$$NaOH \rightarrow Na^+ + OH^-$$

$$MOH \overset{H_2O}{\rightleftharpoons} M^+ + \underline{OH^-}$$

Hydroxide ion

For other Arrhenius bases:

$$B + H_2O \rightleftharpoons BH^+ + OH^- \qquad ex: NH_3$$

An Arrhenius acid base reaction can be represented by:

$$\boxed{H_3O^+ + OH^- \rightleftharpoons 2H_2O}$$

"neutralization"

or, using hydrogen ion instead of hydronium

$$H^+ + OH^- \rightleftharpoons H_2O$$

BRONSTED-LOWRY THEORY

H^+ ions!

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

ACIDS are PROTON DONORS

BASES are PROTON ACCEPTORS

$$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$$

acid

base

conjugate acid of NH_3

conjugate base of HCl

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

... a few examples of conjugate pairs:

Species	Conjugate
NH_3	NH_4^+
H_2O	OH^-
H_2O	H_3O^+
$HC_2H_3O_2$	$C_2H_3O_2^-$

RED for acid

BLUE for base

A generic Bronsted-Lowrey acid.base reaction:

$$HA + B \rightleftharpoons BH^+ + A^-$$

acid

base

conjugate acid of B

conjugate base of HA

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...

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

acid

conjugate base
of HA

$$\boxed{H}C_2H_3O_2 + H_2O \rightleftharpoons H_3O^+ + C_2H_3O_2^-$$

Acetic acid and water

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

base

conjugate acid
of B

$$NH_3 + \boxed{H}_2O \rightleftharpoons \underline{NH_4^+ + OH^-}$$

Ammonia and 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 a acid!

LEWIS THEORY

- Lewis theory treats acid-base chemistry as ELECTRON-TRANSFER chemistry involving pairs of electrons

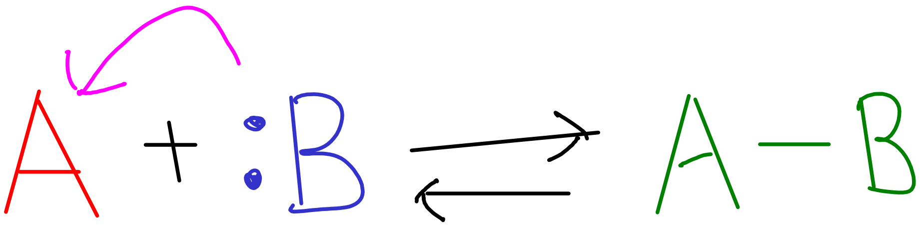
- Lewis acid-base reactions form new covalent bonds (of interest to organic chemists!)

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



Lewis
acid

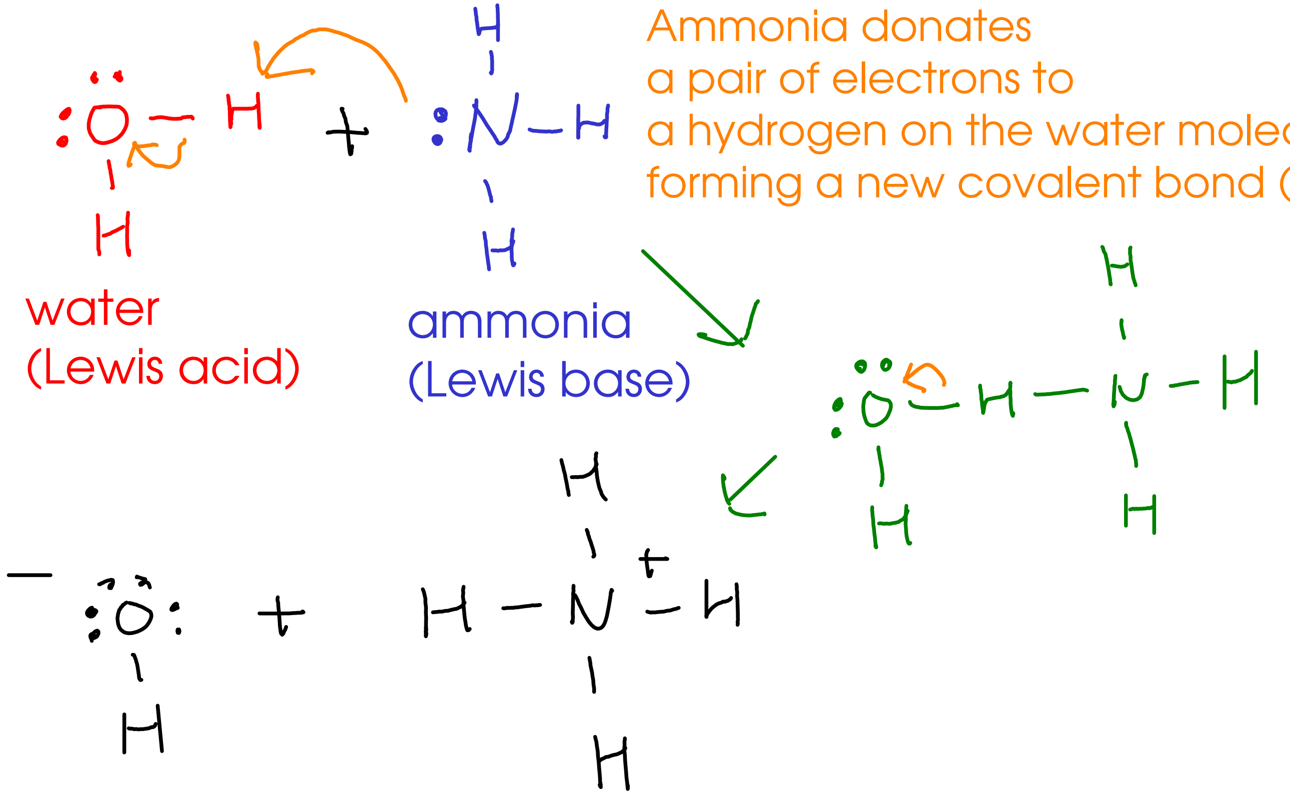
Lewis
base

... 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

$$H_2O + :NH_3 \rightleftharpoons NH_4^+ + OH^-$$



Ammonia donates
a pair of electrons to
a hydrogen on the water molecule,
forming a new covalent bond (and breaking another)

water
(Lewis acid)

ammonia
(Lewis base)

hydroxide ion

ammonium ion

Overall: $H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$

COMPARING THE THEORIES

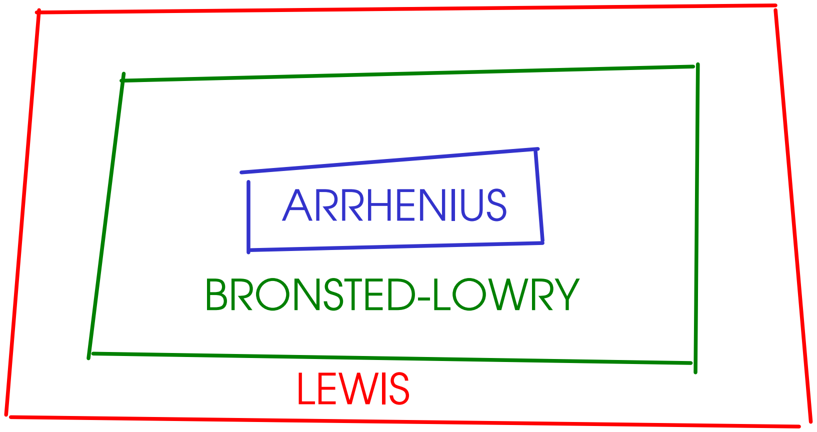
- From Arrhenius to Lewis, the definitions get broader as you go along. In other woeds, the later definitions include MORE SUBSTANCES under the acid/base umbrella.

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.



ARRHENIUS

BRONSTED-LOWRY

LEWIS

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