PRESSURE AND EQUILIBRIUM

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

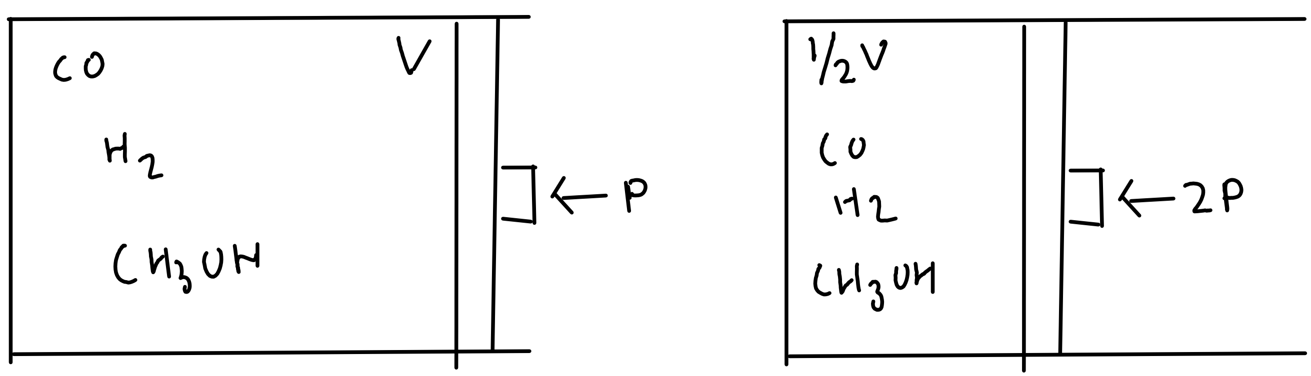
$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

... how might pressure affect this equilibrium?

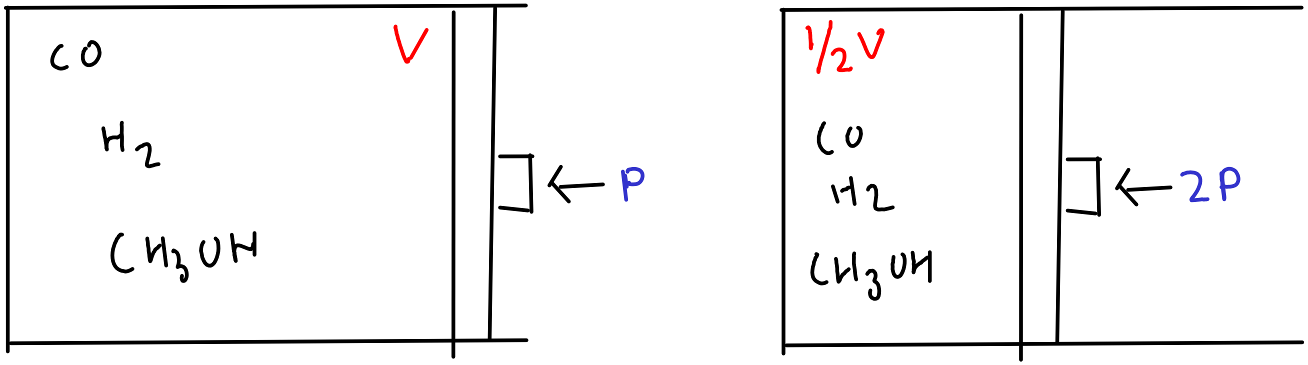
- If the change in pressure CHANGES CONCENTRATIONS, then this equilibrium would be disturbed and Le Chateleir's Principle would apply.

  - 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)

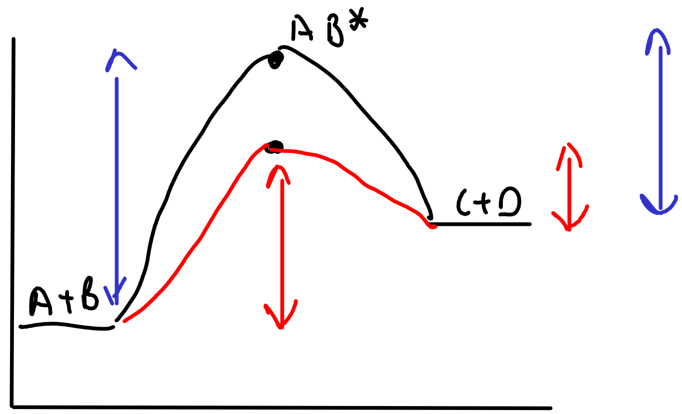
- Changes rate of reaction, too!

... 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 TWO of these theories.

- These theories differ in the way that acids, bases, and their associated reactions are defined, although they cover many of the same reactions.

TWO ACID-BASE THEORIES

1 Arrhenius theory

2 Bronsted-Lowry 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

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

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:

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

$$MOH \overset{H_2O}{\rightleftharpoons} M^+ + \underbrace{OH^-}_{\text{Hydroxide ion}}$$

For other Arrhenius bases:

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

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

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{NH_3} \rightleftharpoons NH_4^+ + Cl^-$$

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:

RED for acid

BLUE for base

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

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!

COMPARING THE THEORIES

- From Arrhenius to B-L, 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 Lowry picture.

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

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

WATER CHEMISTRY

- Water self-ionizes!

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

or

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

This is an equilibrium reaction!

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

(X) = molar concentration of "X"

In aqueous solution, (H_2O) is essentially constant, so we roll that into K.

$$\boxed{K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}}$$

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?

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

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.

$$K_w = [H_3O^+][OH^-] = 1 \times 10^{-14}$$

Solve...

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

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

$$x^2 = 1.0 \times 10^{-14}$$

$$x = 1.0 \times 10^{-7}\,M = [H_3O^+] = [OH^-]$$

"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

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

On a calculator, use $\boxed{\log}$ $\boxed{\cancel{\ln}}$

So,

$$\boxed{pH = -\log_{10}[H_3O^+]}$$

$$\boxed{[H_3O^+] = 10^{-pH}}$$

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

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

"p" NOTATION

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

$$K_w = [H_3O^+][OH^-] = 1.00 \times 10^{-14}$$

becomes ...

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

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