EQUILIBRIUM CALCULATIONS

- We're often interested in figuring out what happens at equilibrium BEFORE we do an experiment!

- What's the problem? Initially, we know only ... INITIAL concentrations. Since these are NOT equilibrium concentrations, we cannot simply plug them into an equilbrium expression and solve.

So how do we find out what the concentrations are at equilibrium if we initially know NONE of them?

- To solve an equilibrium problem, write out the equilibrium constant expression. Then, try to RELATE ALL THE EQUILIBRIUM CONCENTRATIONS TO ONE ANOTHER using the chemical equation.

- It helps to assign a variable based on one of the substances in the reaction, then write the concentrations of the other substances based on that variable. How to do this? Take a look at the following examples...

AgCl: 107.9 + 35.45 = 143.35 g/mol

EXAMPLE: Calculate the grams per liter of silver(i) chloride (AgCl) in a solution that is at equilibrium with solid AgCl.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)\ ;\ K_c = 1.8 \times 10^{-10}$$

$$K_c = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

Assign 'x' to be the cange in silver ion concentration...

Species	[Initial]	Δ	[Equilibrium]
Ag^+	0	+x	x
Cl^-	0	+x	x

Each time we make a silver ion, we also make a chloride ion (see the chemical equation for the 1:1 ratio) ... so every time we make 'x' silvers, we make 'x' chlorides!

$$[Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

Plug in 'x'...

$$(x)(x) = 1.8 \times 10^{-10}$$

$$x^2 = 1.8 \times 10^{-10}$$

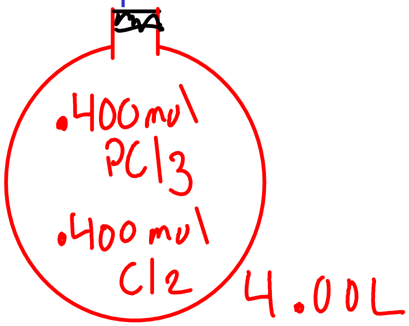
$$x = 1.34 \times 10^{-5}\ ;\ \text{so } [Ag^+] = [Cl^-] = 1.34 \times 10^{-5}\ M$$

The concentration of DISSOLVED AgCl equals the dissolved silver ion concentration ... 'x' ... since every dissolved silver chloride makes a single silver ion.

$$[AgCl]_{dissolved} = 1.34 \times 10^{-5}\ \frac{mol}{L} \times \frac{143.35\ g\ AgCl}{mol\ AgCl} = \boxed{0.0019\ g/L}$$

$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \quad K_c = 49$$

If you add 0.400 moles of each reactant to a 4.00 L reaction vessel, what is the composition of the equilibrium mixture?



Initial conditions

$$K_c = \frac{[PCl_5]}{[PCl_3][Cl_2]} = 49$$

These are EQUILIBRIUM concentrations!

We've defined 'x' to be the change in phosphorus pentachloride concentration

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

$$\frac{[PCl_5]}{[PCl_3][Cl_2]} = \boxed{\frac{(x)}{(0.100 - x)(0.100 - x)} = 49}$$

To solve the problem, we will need to solve this equation for 'x'

Resarrange this equation to make it easier to solve.

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

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

$$(a-b)^2 = a^2 - 2ab + b^2$$

$$\frac{x}{(0.0100 - .200x + x^2)} = 49$$

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

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

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

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

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

$x = \cancel{0.157}$ or 0.0639

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 onlu one of them will be the correct chemical solution.

Species	[Equilibrium]
PCl_5	x
PCl_3	$0.100-x$
Cl_2	$0.100-x$

x=0.157 results in NEGATIVE concentrations for the chlorine and the phosphorus trichloride. This is impossible, so we discard that solution.

Species	[Equilibrium]
PCl_5	x
PCl_3	$0.100 - x$
Cl_2	$0.100 - x$

$x = 0.0639$

Plug in 'x' to find the equilibrium concentrations...

$[PCl_5] = \underline{0.0639\ M}$

$[PCl_3] = 0.100 - x = \underline{0.036\ M}$

$[Cl_2] = 0.100 - x = \underline{0.036\ M}$

Alternatively, we can calculate the composition in moles of each substance ...

PCl_5: $0.0639\ M \times 4.00\ L = 0.256$ mol PCl_5

PCl_3: $0.036\ M \times 4.00\ L = 0.144$ mol PCl_3

Cl_2: $0.036\ M \times 4.00\ L = 0.144$ mol Cl_2

$$\boxed{\begin{array}{l} 0 \text{ mol } PCl_5 \\ 0.400 \text{ mol } PCl_3 \\ 0.400 \text{ mol } Cl_2 \end{array}} \xrightarrow{K_c = 49} \boxed{\begin{array}{l} 0.256 \text{ mol } PCl_5 \\ 0.144 \text{ mol } PCl_3 \\ 0.144 \text{ mol } Cl_2 \end{array}}$$

122 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.

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

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

To solve this, express all these concentrations in terms of one variable!

We let 'x' equal the change in nitrogen concentration

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	$+2x$	$2x$

$$\frac{[NO]^2}{[N_2][O_2]} = \boxed{\frac{(2x)^2}{(0.10625-x)(0.10625-x)} = 0.0123}$$

We must solve this expression for 'x' to solve the problem.

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

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

You can solve this as a quadratic, or you can take the (simpler) route of taking the square root of both sides...

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

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

$$\times(.10625-x)$$
$$\div(0.1109053651)$$

$$18.03339269x = 0.10625 - x$$

$$19.03339269x = 0.10625$$

$$x = 0.005582943$$

$$\boxed{\begin{aligned} N_2 &: 0.10625 - x = 0.101\ M \\ O_2 &: 0.10625 - x = 0.101\ M \\ NO &: 2x = 0.0112\ M \end{aligned}}$$

Since Kc = 0.0123 (a small value), we expect REACTANTS to dominate at equilibrium ... and they do!

PRESSURE AND EQUILIBRIUM

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

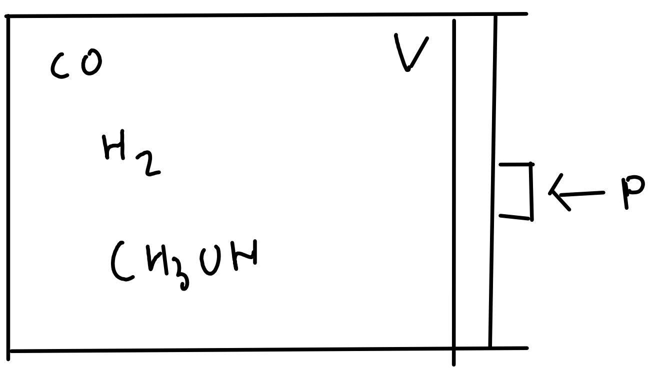
$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

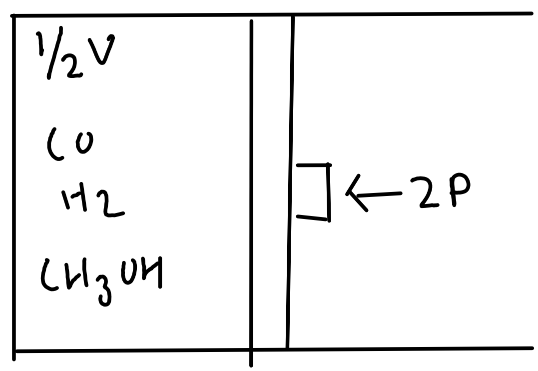
... how might pressure affect this equilibrium?

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

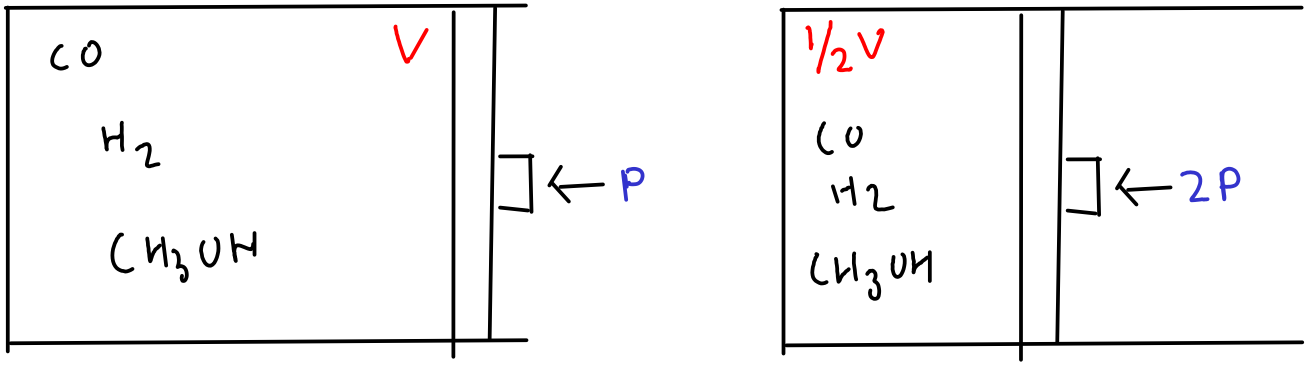
  - Adding an INERT GAS would change pressure, but would it change concentration of the gases? NO - so addition of argon would have no effect on the equilibrium!

    - 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)

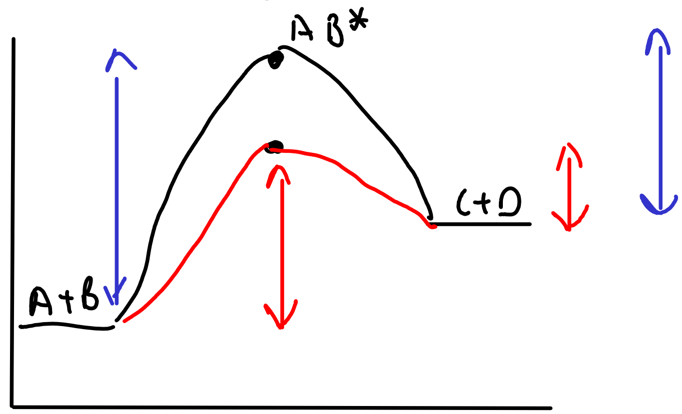
- Changes rate of reaction, too!

... 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.