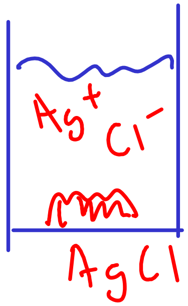
EXAMPLE: Calculate the grams per liter of silver(i) chloride (AgCl) in a solution that is at equilibrium with solid AgCl.

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



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

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

Assign a variable, 'x', to equal the change in concentration of the silver(I) ion...

Each time we make a silver(I) ion, we also make a chloride ion. See the equation ... there's a 1:1 ratio of silver to chloride.

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

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

Subsitiute the variable 'x' into the equilibrium experssion, then solve for 'x'.

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

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

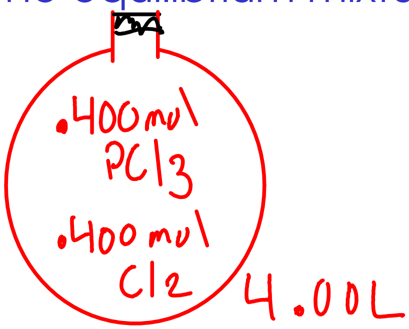
The concentration of DISSOLVED AgCl also equals 'x' ... since for every dissolved AgCl you have a dissolved Ag.ion:

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

Equivalent to 1.9 ppm (parts per million). ppm is same as mg/L for dilute aqueous solutions

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

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



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

These concentrations are molar concentrations AT EQUILIBRIUM!

Initial conditions

SPECIES	INITIAL CONC	CHANGE	EQUILIBRIUM CONC
PCl_3	$\frac{0.400\ mol}{4.00\ L} = 0.100\ M$	$-x$	$0.100 - x$
Cl_2	$\frac{0.400\ mol}{4.00\ L} = 0.100\ M$	$-x$	$0.100 - x$
PCl_5	$0\ M$	$+x$	x

We've defined 'x' to be the change in concentration of phosphorus trichloride!

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

To solve the problem, we must solve this expression for 'x'.

Rearrange the experssion to make it easuer to solve. Usually, we try to isolate 'x'.

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

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

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

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

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

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

$$0 = 0.49 - 10.8x + 49x^2 \quad \text{or} \quad \underbrace{49}_{a}x^2 \underbrace{-10.8}_{b}x + \underbrace{0.49}_{c} = 0$$

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

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

$$x = \cancel{0.157} \quad \underline{\text{OR}} \quad 0.0639$$

This value of 'x' results in a NEGATIVE concentration for both phosphorus trichloride and chlorine. Since that's impossible, we discard this solution. It does not make chemical sense.

This equation is second order in 'x'. ... or in other words, it;s a 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	INITIAL CONC	CHANGE	EQUILIBRIUM CONC
PCl_3	$\frac{0.400\text{ mol}}{4.00\text{ L}} = 0.100\text{ M}$	$-x$	$0.100 - x$
Cl_2	$\frac{0.400\text{ mol}}{4.00\text{ L}} = 0.100\text{ M}$	$-x$	$0.100 - x$
PCl_5	0 M	$+x$	x

$x = 0.0639$

EQUILIBRIUM CONCENTRATIONS

MOLES of each species at equilibrium

$[PCl_3] = 0.100 - x = 0.036\text{ M}$ $\times 4.00\text{ L} = 0.144\text{ mol } PCl_3$

$[Cl_2] = 0.100 - x = 0.036\text{ M}$ $\times 4.00\text{ L} = 0.144\text{ mol } Cl_2$

$[PCl_5] = x = 0.0639\text{ M}$ $\times 4.00\text{ L} = 0.256\text{ mol } PCl_5$

Quick comparison of initial and equilibrium states:

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

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, we must express all of these concentrations in terms of one variable.

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

We let 'x' equal the change in concentration of nitrogen gas!

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

We need to solve this expression for 'x' to solve this 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 by either using the quadratic equation (like the last one), or - more simply - just take the square root of both sides.

$$\frac{2x}{0.10625-x} = 0.110905365\,1$$

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

$$18.03339269x = 0.10625 - x$$

$$19.03339269x = 0.10625$$

$$x = 0.005582294\,3$$

<-- Now use this value of 'x' to find the equilibrium concentrations!

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

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

We know Kc = 0.0123, so we expect REACTANTS to dominate at equilibrium. (They do!)

PRESSURE AND EQUILIBRIUM

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

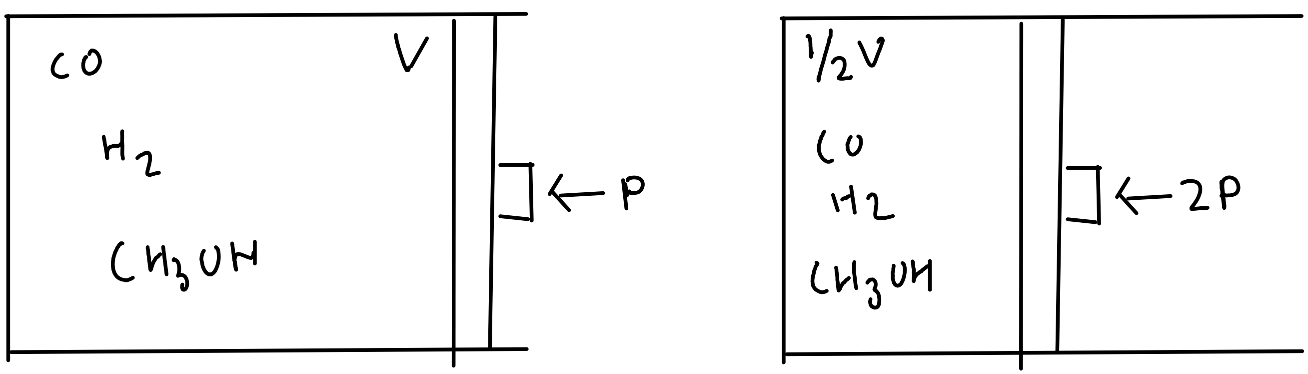
$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

... how might pressure affect this equilibrium?

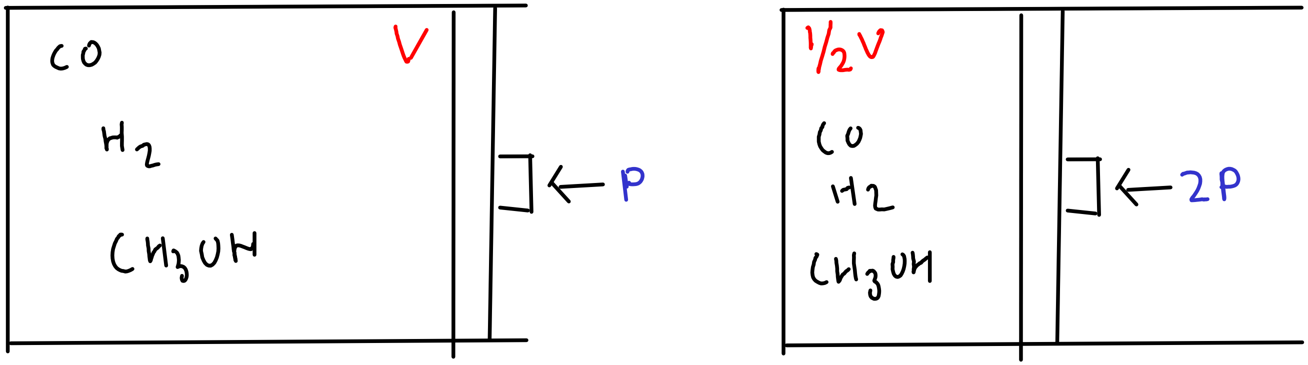
- If the change in pressure CHANGES CONCENTRATIONS, then this equilibrium would be disturbed and Le Chateleir's Principle would apply.

  - 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= $\dfrac{2}{(2)(2)^2} = \dfrac{1}{4}$

$Q < K_c$, 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)

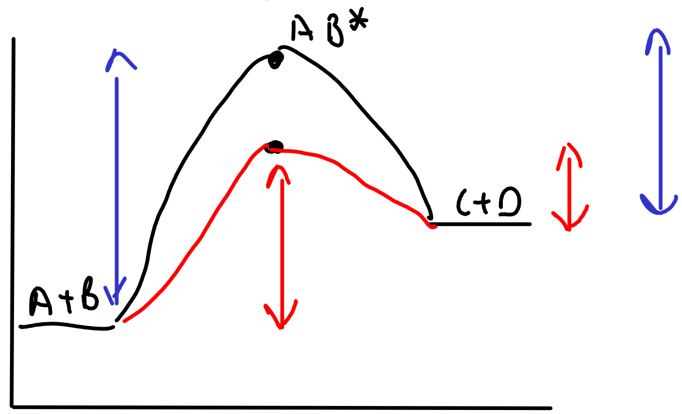
   - Changes rate of reaction, too!

   ... 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.