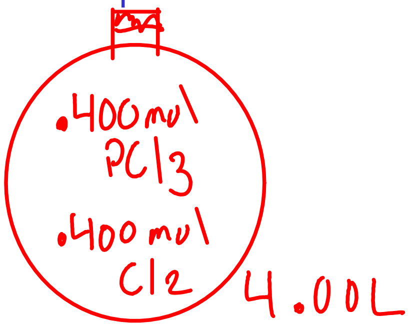
$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \quad K_c = 49$$

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

Start with the equilibrium expression:

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

These concentrations are EQUILIBRIUM concentrations

SPECIES	INITIAL CONCENTRATION	Δ	EQUILIBRIUM CONCENTRATION
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	$+x$	x

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

To solve the problem, we need to solve this expression for 'x'!

Rearrange this equation in an attempt to make it easier to solve, Usually, that means isolating 'x'.

$$\frac{x}{(.100-x)(.100-x)} = 49$$

$$\frac{x}{(.100-x)^2} = 49$$

$$x = 49(.100-x)^2$$

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

$$x = 49(0.0100 - .200x + x^2)$$

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

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

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

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

$x = \cancel{0.157}$ OR 0.0639

This value for 'x' results in NEGATIVE equilibrium concentrations for both phosphorus trichloride and chlorine gas. Negative concentrations are physically impossible, so we throw out this solution.

This equation is a QUADRATIC equation:

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

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

Each quadratic equation has TWO solutions. However, only ONE of these solutions makes chemical sense!

	Initial	Δ	Equilibrium
$[PCl_5]$	0	$+x$	x
$[Cl_2]$	$\frac{.400 \text{ mol}}{4.00 \text{ L}} = .100$	$-x$	$0.100 - x$
$[PCl_3]$	$\frac{.400 \text{ mol}}{4.00 \text{ L}} = .100$	$-x$	$0.100 - x$

$x = 0.0639$ M

$[PCl_5] = x = 0.0639$ M $\times 4.00$ L $= .256$ mol PCl_5

$[Cl_2] = 0.100 - x = 0.0361$ M $\times 4.00$ L $= .144$ mol Cl_2

$[PCl_3] = 0.100 - x = 0.0361$ M $\times 4.00$ L $= .144$ mol PCl_3

Concentrations at equilibrium

Number of moles in reaction vessel at equilibrium

Quick comparison of initial and equilibrium states:

INITIAL STATE		EQUILIBRIUM STATE
0.400 mol PCl_3	→	0.144 mol PCl_3
0.400 mol Cl_2	$K_c = 49$	0.144 mol Cl_2
0 mol PCl_5		0.256 mol PCl_5

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.

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

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

We need to express all of these EQUILBIRIUM concentrations in terms of a single variable.

SPECIES	INITIAL CONCENTRATION	Δ	EQUILIBRIUM CONCENTRATION
NO	0	$+2x$	$2x$
N_2	$\frac{0.850\text{ mol}}{8.00\text{ L}} = 0.10625\text{ M}$	$-x$	$0.10625 - x$
O_2	$\frac{0.850\text{ mol}}{8.00\text{ L}} = 0.10625\text{ M}$	$-x$	$0.10625 - x$

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

We need to solve this expression for 'x' to find the equilibrium concentrations.

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

Solve for x by taking the square root of both sides, then isolating 'x'.

SPECIES	EQUILIBRIUM CONCENTRATION
NO	$2x$
N_2	$0.10625 - x$
O_2	$0.10625 - x$

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

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

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

$$2x = 0.110905365(0.10625-x)$$

$$2x = 0.011783695 - 0.110905365x$$

$$2.110905365x = 0.011783695$$

$$x = 0.005582$$

$[NO] = 2x = 0.0112\ M$

$[N_2] = 0.10625 - x = 0.101\ M$

$[O_2] = 0.10625 - x = 0.101\ M$

Since Kc = 0.0123, we expect the reactants to dominate at equilibrium. This agrees with our calculated numbers!

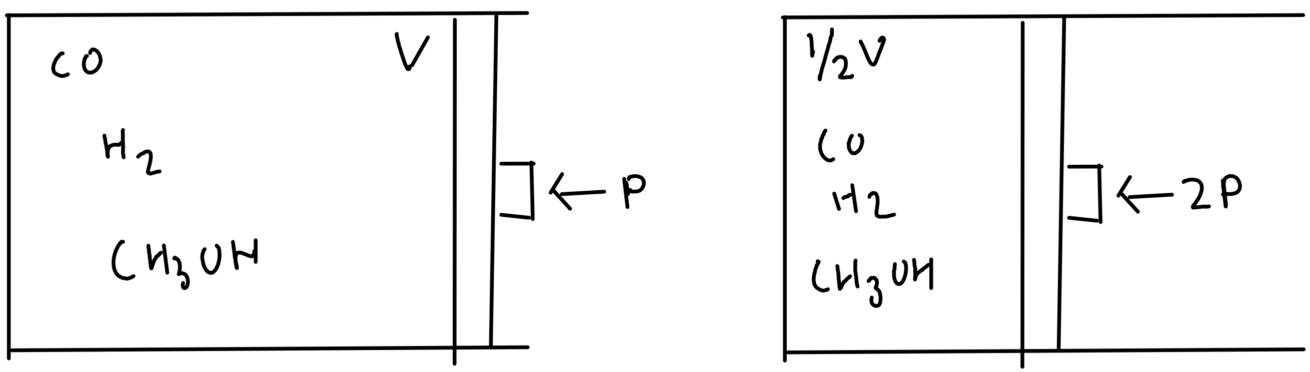
PRESSURE AND EQUILIBRIUM

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

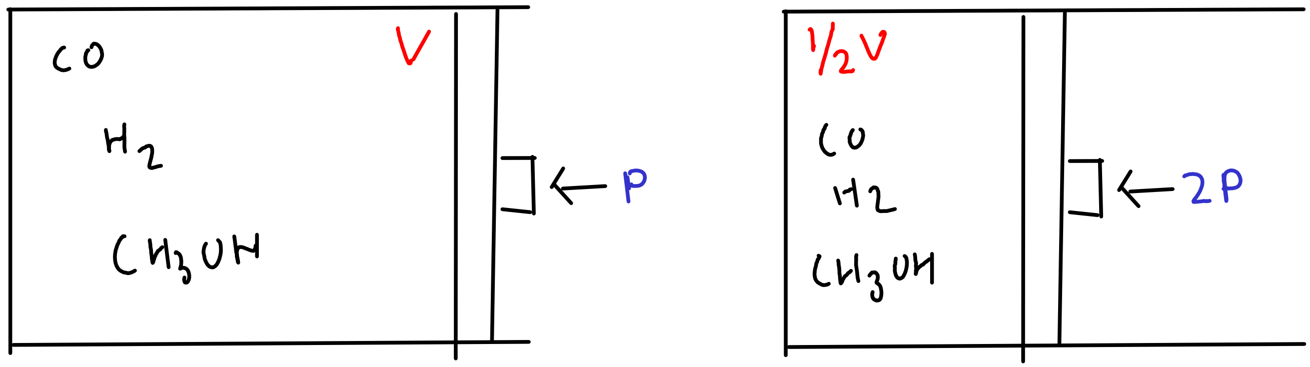
$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

... 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.

FACTORS THAT MAY AFFECT EQUILBRIUM

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

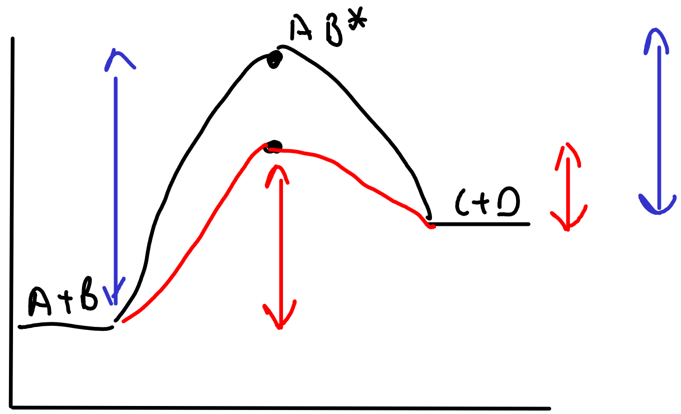
- Changes rate of reaction, too!

... 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 be reached faster.



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.