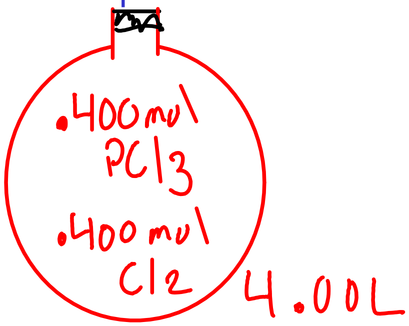
$$PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g) \quad K_c = 49$$

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




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

These cponcentrations are molar concentrations AT EQUILIBRIUM (in other words, they are DIFFERENT from initial concentrations)

Initial conditions

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

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

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

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

Rearrange this to make it easier to solve!

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

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

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

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

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

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

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

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

So,

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

$x = \sout{0.157}$ or $0.0639$

This value of 'x' resultrs in NEGATIVE concentrations for both reactants. Since negative concentrations are not possible, we throw out this answer.

This equation is second order in 'x' ... in other words, it's a QUADRATIC equation.

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

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

Each quadratic equation has TWO SOLUTIONS. Only ONE of these solutions will work for the CHEMICAL problem. (The second solution will not make chemical sense)

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

$x = 0.0639$

So,

Equilibrium concentrations

Number of moles of each substance

$[PCl_3] = 0.100 - x = 0.036\,M \times 4.00\,L = 0.14\,mol\ PCl_3$

$[Cl_2] = 0.100 - x = 0.036\,M \times 4.00\,L = 0.14\,mol\ Cl_2$

$[PCl_5] = x = 0.064\,M \times 4.00\,L = 0.26\,mol\ PCl_5$

Quick comparison of initial and equilibrium states

| | | |
|---|---|---|
| 0.400 mol $PCl_3$ | $K_c = 49$ → | 0.14 mol $PCl_3$ |
| 0.400 mol $Cl_2$ | | 0.14 mol $Cl_2$ |
| 0 mol $PCl_5$ | | 0.26 mol $PCl_5$ |

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.

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

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

We need to express each of these conrentrations in terms of a single variable, then solve.

| Species | [Initial] | $\Delta$ | [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 | $+2x$ | $2x$ |

Let 'x' equal the cnange in concetration of nitrogen gas.

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

We need to solve this expression for 'x' to complete the problem.

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

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

Solve by using the quadratic equation, OR solve by taking the square root of both sides to simplify the equation.

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

$$0.011783695 - 0.1109053651x = 2x$$

$$0.011783695 = 2.1109053651x$$

$$x = 0.005582943$$

Since the value of Kc is low (0.0123), we expect REACTANTS to dominate at equilibrium.

They do!

$N_2$: $0.10625 - x = 0.101\ \underline{M}$

$O_2$: $0.10625 - x = 0.101\ \underline{M}$

$NO$: $2x = 0.0112\ \underline{M}$

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

# PRESSURE AND EQUILIBRIUM

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

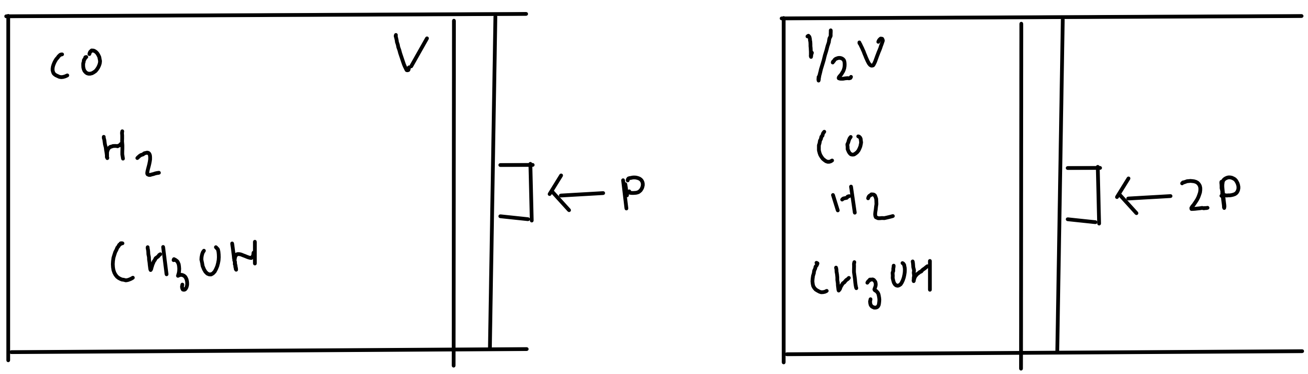
$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

... how might pressure affect this equilibrium?

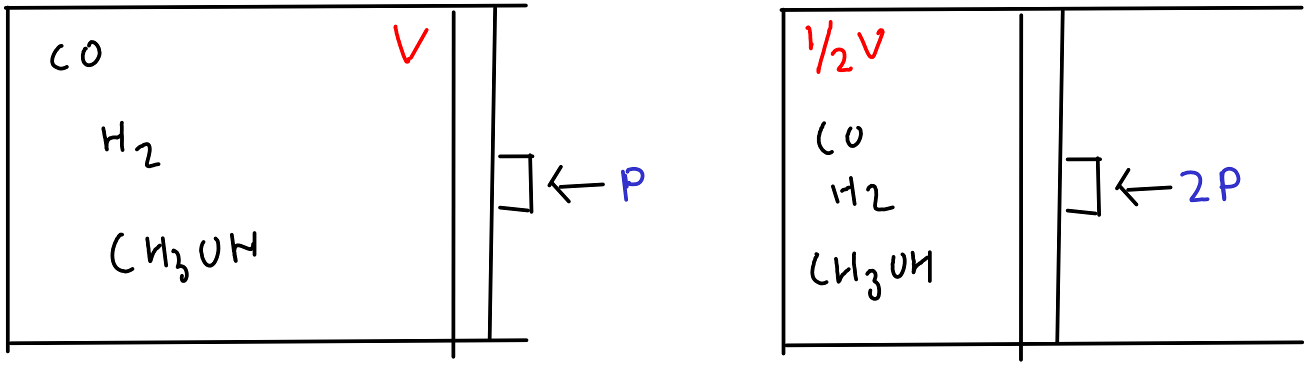
- If the change in pressure CHANGES CONCENTRATIONS, then this equilibrium would be disturbed and Le Chateleir's Principle would apply.

  - 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.