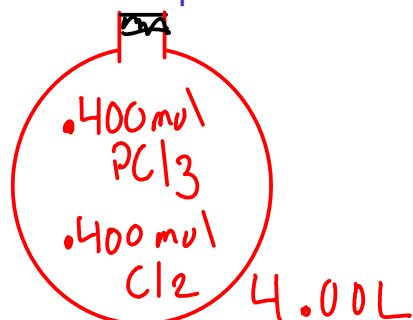


If you add 0.400 moles of each reactant to a 4.00 L reaction vessel, what is the concentration of each species in the equilibrium mixture?



$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = 49$$

We need to relate all three of these concentrations to a single variable to solve the problem.

Initial conditions

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

Let "x" equal the change in concentration of phosphorus trichloride...

$$\frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{x}{(0.100 - x)(0.100 - x)} = 49$$

To solve the problem now, we need to solve this equation for "x"

This is a second-order equation in "x" ...

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

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

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

$$\frac{x}{(0.100 - 0.200x + x^2)} = 49$$

$$x = 49(0.100 - 0.200x + x^2)$$

$$x = 0.490 - 9.80x + 49x^2$$

$$0 = 49x^2 - 10.8x + 0.490$$

$$a = 49 \quad b = -10.8 \quad c = 0.490$$

$$x = \frac{+10.8 \pm \sqrt{(-10.8)^2 - 4(49)(0.490)}}{2(49)} = \frac{10.8 \pm \sqrt{20.6}}{98}$$

$$x = \cancel{0.157} \text{ or } \underline{0.0639}$$

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 only one of them will be the correct chemical solution.

This value of "x" gives us negative concentrations for both phosphorus trichloride and chlorine, which is a physically impossible situation (violates conservation of mass). Therefore the other solution ... 0.0639 ... must be the correct one.

Initial conditions

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

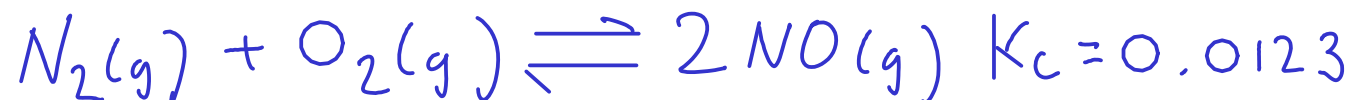
$x = 0.0639$ Now plug the correct value for "x" into the expressions from our chart to get the equilibrium concentrations ...

$$[\text{PCl}_3] = 0.100 - 0.0639 = 0.036 \text{ M PCl}_3$$

$$[\text{Cl}_2] = 0.100 - 0.0639 = 0.036 \text{ M Cl}_2$$

$$[\text{PCl}_5] = 0.0639 \text{ M PCl}_5$$

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.



$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = 0.0123$$

To solve, we must express all three concentrations in terms of a single variable.

| 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 | $+2x$ | $0 + 2x = 2x$ |

Let "x" equal the decrease in nitrogen gas concentration

$$\frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(2x)^2}{(0.10625 - x)(0.10625 - x)} = 0.0123$$

Now we need to solve this equation for "x" to proceed.

This is (another) second-order equation!

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

Since this is second-order, you CAN solve this one using the quadratic equation ... if you rearrange it. But for this one, there IS another way ...

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

Take the square root of both sides!

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

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

$$2x = 0.011783695 - 0.1109053651x$$

$$2.1109053651x = 0.011783695$$

$$x = 0.0055822943$$

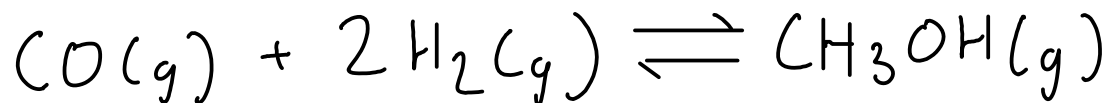
Since we've solved for "x", use this to find the concentrations

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

| Species | [Equilibrium] |
|---------|---------------|
| N_2 | $0.10625 - x$ |
| O_2 | $0.10625 - x$ |
| NO | $0 + 2x = 2x$ |

These look good ... since K_c is small, we don't expect much NO!

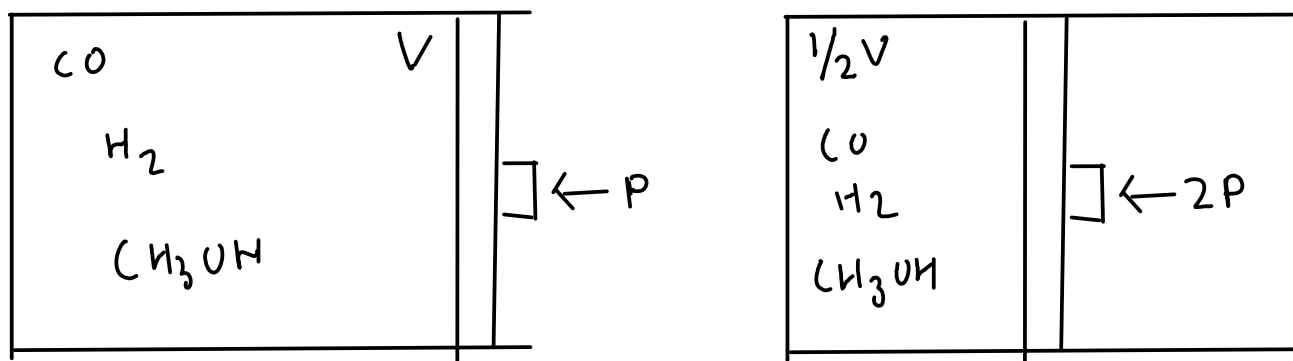
- Pressure can affect a GAS-PHASE equilibrium ... sometimes. How?



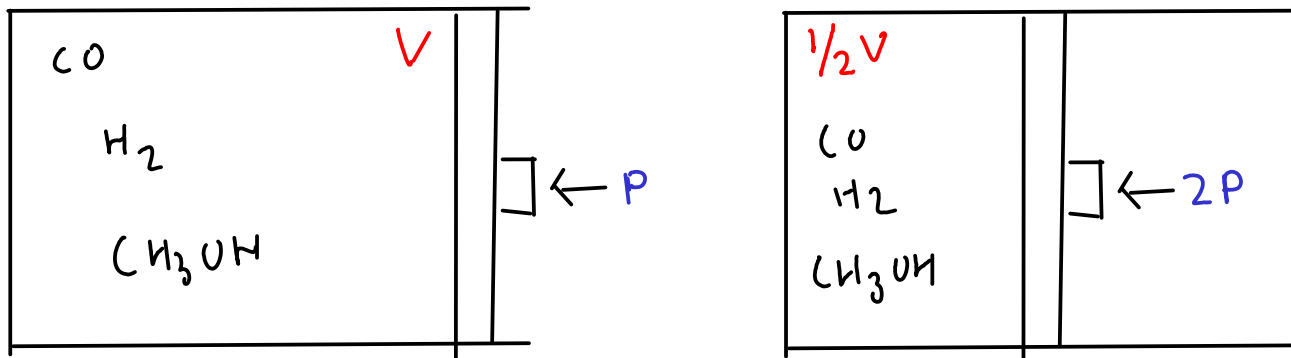
... how might pressure affect this equilibrium?

- If the change in pressure CHANGES CONCENTRATIONS, then this equilibrium would be disturbed and Le Chateleur'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!

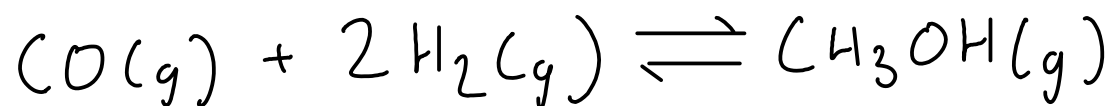
- What about COMPRESSION?



... compression increases pressure by DECREASING total volume.



... but this volume change affects ALL concentrations the same way. In this example, each concentration is DOUBLED.



$$K_c = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{(1)}{(1)(1)^2} = 1$$

For simplicity,
let's assume
 $K_c = 1$, and all
concs = 1M

Doubling
concentrations
gives $Q =$

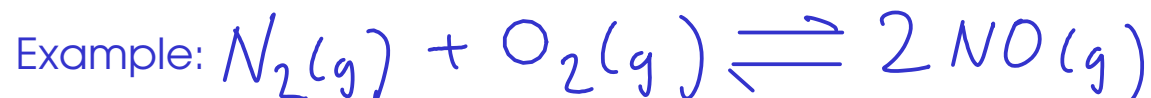
$$\frac{2}{(2)(2)^2} = \frac{1}{4}$$

$Q < K_c$, 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.



... would not respond to a pressure change.

¹¹⁹ FACTORS THAT MAY AFFECT EQUILIBRIUM

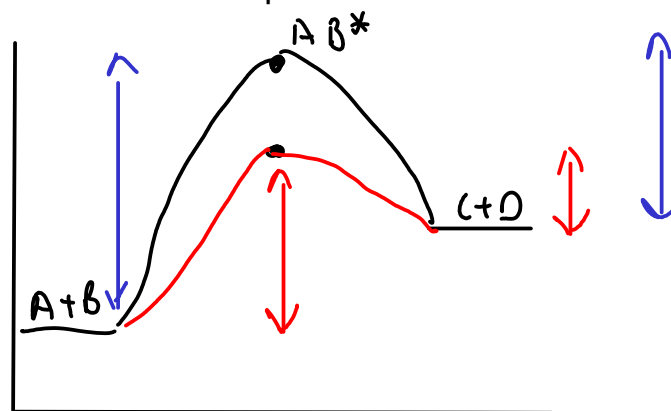
① TEMPERATURE (effect depends on whether reaction is endothermic or exothermic)

- Changes rate of reaction, too!
... changes K_c

② PRESSURE - only for gas-phase reactions which have different numbers of moles of gas on each side of the equilibrium. Otherwise, no effect.

... no change of K_c

③ CATALYSTS - do NOT affect equilibrium, but make the equilibrium 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 Chateleur's Principle applies for changing concentrations. An equilibrium will shift to counteract a change in concentration of reactant or product.

... doesn't change K_c .