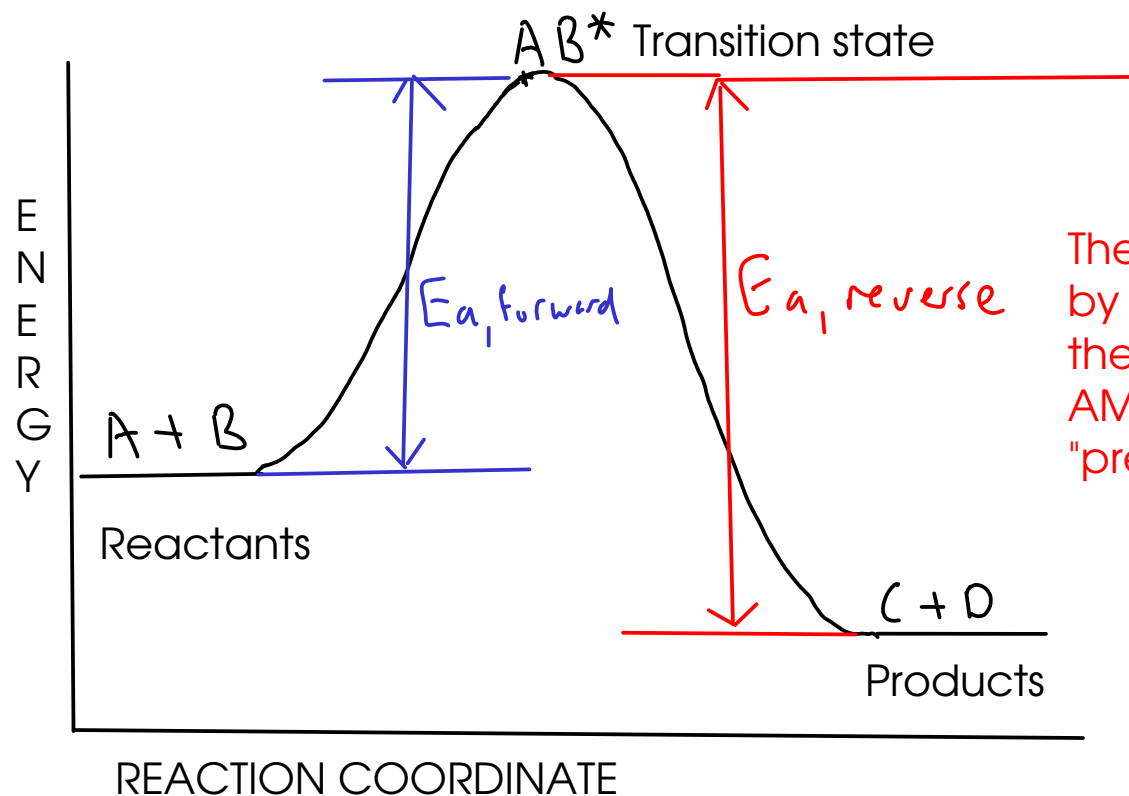
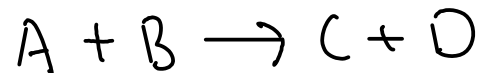


WHAT KEEPS A REACTION FROM GOING BACKWARDS?



... what keeps the reaction on the right from occurring?

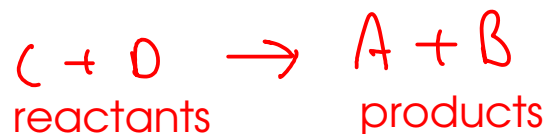


The reverse reaction is "prevented" by an activation energy barrier - the same thing (if not the same AMOUNT of energy) that "prevents" the forward reaction!

So what really happens during a reaction? Both forward and reverse reactions occur!

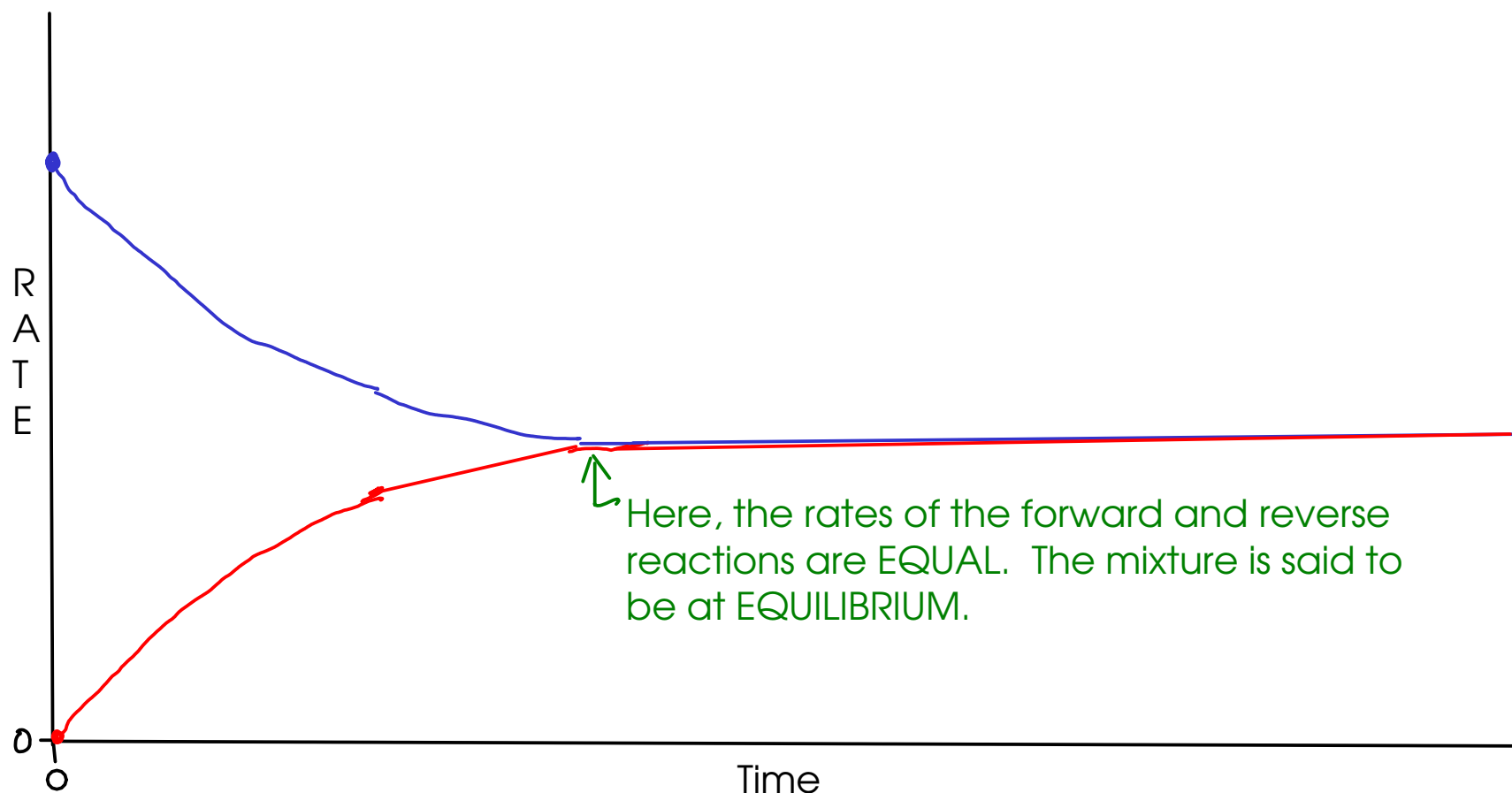


$$\text{Rate} = k_f [A][B]$$



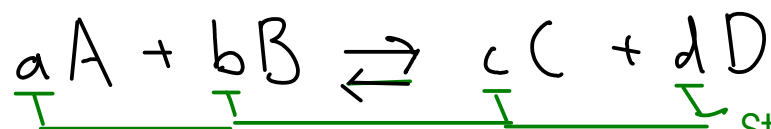
$$\text{Rate} = k_r [C][D]$$

- Let's look at the RATES of both the forward and reverse reactions over time.



- Initially, the mixture is all A and B. As C and D are formed, the rate of the reverse reaction increases while the rate of the forward reaction decreases. Eventually, these rates become equal.

- At EQUILIBRIUM, the concentrations of A, B, C, and D stop CHANGING. The reaction doesn't stop, but it appears stopped to an outside observer.



Stoichiometric coefficients

- Double-headed arrow is often used to show that both the forward and reverse reactions are important.

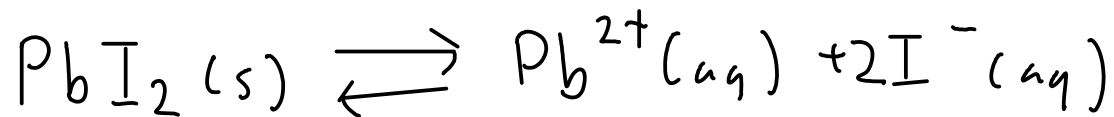
$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

[ ] : molar concentrations of reactants and products AT EQUILIBRIUM.

Equilibrium constant (concentration based)

- At equilibrium, the ratio above equals a constant number - the EQUILIBRIUM CONSTANT. The equilibrium constant depends on TEMPERATURE, but not on other factors.

- Not all reactants and products are included in the equilibrium constant expression!



$$K_c = \frac{[\text{Pb}^{2+}][\text{I}^{-}]^2}{[\text{PbI}_2]}$$

Since the concentration of SOLID lead(II) iodide is fixed by the crystal structure of the solid and does not change over the course of the reaction, we "fold it" into the equilibrium constant.

$$K_c = [\text{Pb}^{2+}][\text{I}^{-}]^2 = 6.5 \times 10^{-9}$$

- Species whose CONCENTRATIONS do not change do not appear in the equilibrium constant expression. PURE SOLIDS and PURE LIQUIDS. Also, bulk SOLVENTS (like water when dealing with a reaction that takes place in water).



$$K_c = \frac{[\text{H}_3\text{O}^{+}][\text{C}_2\text{H}_3\text{O}_2^{-}]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.7 \times 10^{-5}$$

Since water is the solvent, there's enough of it so that the reaction doesn't really change the concentration of the water itself.

$[\text{H}_2\text{O}] = ?$

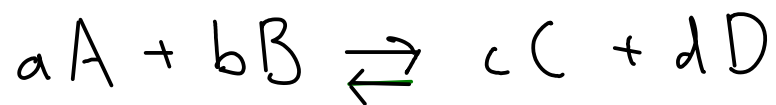
1 g/mL, 1 L water  $\approx$  1000 g  $\text{H}_2\text{O}$

$$1000 \text{ g } \text{H}_2\text{O} \times \frac{\text{mol}}{18.02 \text{ g}} \approx 55.5 \text{ mol } \text{H}_2\text{O} / \text{L} \approx 55.5 \text{ M}$$

## WHAT DOES AN EQUILIBRIUM CONSTANT TELL US?

- ① - Whether the final reaction mixture consists of mainly products or mainly reactants. In other words, which side of the reaction is "favored". (*"extent" of reaction*)
- ② - Whether a reaction will proceed to the left or to the right when the reaction is not yet at equilibrium.
- ③ - With more math, we can actually determine the final composition of an equilibrium mixture from the initial amount of reactant present WITHOUT doing an experiment!

WHICH IS FAVORED? PRODUCT OR REACTANT?



$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$



$$K_c = \frac{[H_3O^+][Cl_2H_3O_2^-]}{[HCl_2H_3O_2]} = 1.7 \times 10^{-5}$$

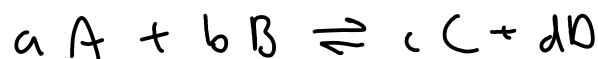
To get a small value like this one, the DENOMINATOR of the equilibrium expression must be a lot larger than the NUMERATOR.

Since REACTANTS are the denominator of this fraction, this reaction favors REACTANTS at equilibrium!

- If  $K_c$  is small ( $\ll 1$ ), then REACTANTS are favored at equilibrium
- If  $K_c$  is large ( $\gg 1$ ), then PRODUCTS are favored at equilibrium.

## HOW TO TELL IF A REACTION IS AT EQUILIBRIUM?

- Use REACTION QUOTIENT (Q)



$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Reaction quotient = equilibrium expression using NON-EQUILIBRIUM concentrations.

- If  $Q = K_c$ , then reaction is at equilibrium.
- If  $Q < K_c$ , then reaction is NOT at equilibrium and proceeds to the right, forming more products.
- If  $Q > K_c$ , then reaction is NOT at equilibrium and proceeds to the left, forming more reactants.



$$[\text{NOBr}] = 0.0720 \text{ M}, [\text{NO}] = 0.0162 \text{ M}, [\text{Br}_2] = 0.0123 \text{ M}$$

Is mix at equilibrium? If not, which direction will reaction proceed?

$$Q = \frac{[\text{NO}]^2 [\text{Br}_2]}{[\text{NOBr}]^2} = \frac{(0.0162)^2 (0.0123)}{(0.0720)^2} = 6.23 \times 10^{-4}$$

$$Q > K_c$$

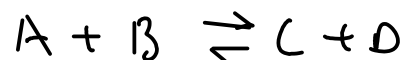
$$6.23 \times 10^{-4} > 3.07 \times 10^{-4}$$

so reaction proceeds to LEFT...

## MODIFYING EQUILIBRIUM

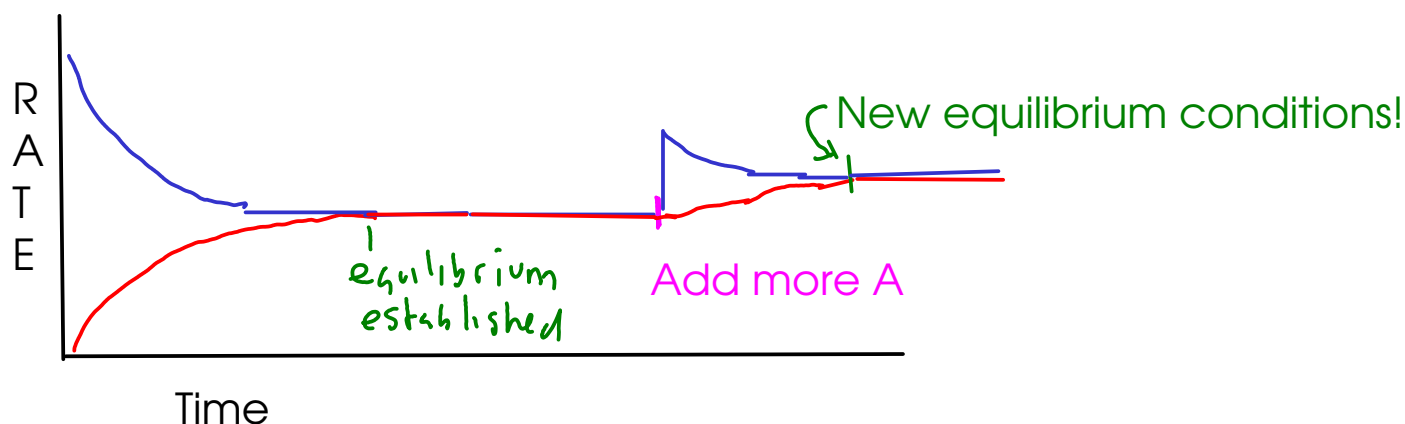
- Remember, at equilibrium the reaction has not actually STOPPED. Both forward and reverse processes are still happening - just at the same rate so there's no overall concentration change.
- If you do something to the reaction mixture that changes the rates of the forward or the reverse reaction (or sometimes BOTH), the mixture will no longer be at equilibrium.

Simplest case is to add or remove a substance, changing its concentration.



$$\text{Rate}_{\text{fwd}} = k_{\text{F}}[A][B]$$

$$\text{Rate}_{\text{rev}} = k_{\text{r}}[C][D]$$



- After adding A, the rate of the forward reaction increased. As more C and D were produced by the (faster) forward reaction, the forward reaction and reverse reaction came back to equilibrium, but at a new set of conditions.
- The addition of A caused our equilibrium to SHIFT towards the RIGHT - consuming some of the extra A to form more products (C and D).



- LE CHATELEIR'S PRINCIPLE states that if an equilibrium is disturbed, it will SHIFT in such a way as to counteract the disturbance and restore equilibrium.

For concentrations:

- \* Increasing the concentration of a REACTANT will cause the equilibrium to shift to the RIGHT, making more products.
  - \* Decreasing the concentration of a REACTANT will cause the equilibrium to shift to the LEFT, making more reactants.
- 
- \* Increasing the concentration of a PRODUCT will cause the equilibrium to shift to the LEFT, making more reactants.
  - \* Decreasing the concentration of a PRODUCT will cause the equilibrium to shift to the RIGHT, making more products.

↑ This one can be used to DRIVE a reaction to produce product, even if the  $K_c$  value is NOT favorable.

- TEMPERATURE can also cause equilibrium shifts. These temperature-caused shifts can be easily illustrated with Le Chaleleir's principle.

endothermic reaction:



- Heat, here, is represented as if it's a reactant!
- If temperature INCREASES, the equilibrium shifts to the RIGHT, making more products.
- If temperature DECREASES, the equilibrium shifts to the LEFT, making more reactants.

exothermic reactions:



- In the exothermic case, heat is a product!
- If temperature INCREASES, then the equilibrium shifts to the LEFT, making more reactants.
- If temperature DECREASES, then the equilibrium shifts to the RIGHT, making more products.

- Optimization:

- \* For ENDOTHERMIC reactions, run as hot as possible. You make MORE products FASTER.
- \* For EXOTHERMIC reactions, you want to run the reaction cooler (for more products), but not so cool as to make the reaction slow!

## 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 equilibrium 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...

$$\text{AgCl}: 107.9 + 35.45 = 143.35 \text{ g/mol}$$

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



We need to calculate the concentration of DISSOLVED AgCl ... which basically equals the concentration of the silver (or chloride) ion.



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

We need to solve for (Ag+)

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{Ag}^+$	0	+x	$0 + x = x$
$\text{Cl}^-$	0	+x	$0 + x = x$

Assign variable "x" to equal the change in concentration of silver ion!

Every time we make an Ag+ ion, we make a Cl- ion!

Plug equilibrium concentrations into the equilibrium expression...

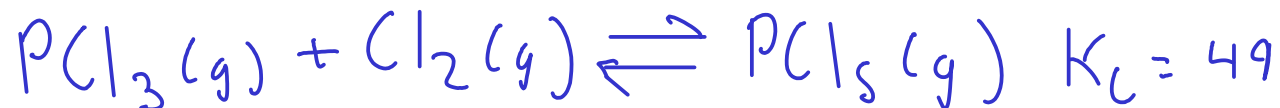
$$1.8 \times 10^{-10} = (x)(x)$$

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

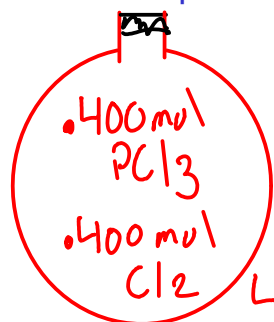
$$1.34 \times 10^{-5} = x = [\text{Ag}^+]$$

Convert units ... We know (Ag+) = (AgCl)dissolved, but we need it in grams per liter...

$$\frac{1.34 \times 10^{-5} \text{ mol AgCl}}{\text{L}} \times \frac{143.35 \text{ g AgCl}}{\text{mol AgCl}} = 0.0019 \text{ g AgCl/L}$$



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?



4.00 L

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

Like last example, set up a chart for your information ...

Initial conditions

Species	[Initial]	Δ	[Equilibrium]
PCl <sub>5</sub>	0	+X	X
PCl <sub>3</sub>	$\frac{0.400 \text{ mol}}{4.00 \text{ L}} = 0.100$	-X	0.100 - X
Cl <sub>2</sub>	$\frac{0.400 \text{ mol}}{4.00 \text{ L}} = 0.100$	-X	0.100 - X

Assign "x" to equal the change in phosphorus pentachloride concentration ...

Plug equilibrium concentrations into equilibrium expression ...

$$49 = \frac{X}{(0.100 - X)(0.100 - X)} \quad ; \quad 49 = \frac{X}{(0.100 - X)^2}$$

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

Let's rearrange this in the form of a quadratic...

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

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

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

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

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

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

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

Use quadratic formula...

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

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

While 0.157 works as a solution to the quadratic equation, it won't work in the CHEMICAL problem because it causes the concentrations of phosphorus trichloride and chlorine to both be negative at equilibrium ... which violates CONSERVATION OF MASS!

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.

Plug  $x=0.0639$  into the expressions we have for equilibrium concentration...

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{PCl}_5$	0	$+X$	$X$
$\text{PCl}_3$	$\frac{0.400 \text{ mol}}{4.00 \text{ L}} = 0.100$	$-X$	$0.100 - X$
$\text{Cl}_2$	$\frac{0.400 \text{ mol}}{4.00 \text{ L}} = 0.100$	$-X$	$0.100 - X$

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

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

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

Since the equilibrium constant was 49 ( $>1$ ), we expected to see more product (phosphorus pentachloride) in the equilibrium mixture than reactants ... and that's what we DID see!