



## Pre-Health Post-Baccalaureate Program Study Guide and Practice Problems

Course: CHM2046

Textbook Chapter: 17 (Silberberg 6e)

Topics Covered: CHM2045 Review:

Gas-phase & Heterogeneous  
Equilibria

Le Chatelier's Principle

## Review and Preview

Last week, we talked about kinetics (covered at the end of CHM2045), which describes how the concentrations of reactants and products change as a reaction proceeds. The reaction gives the **rate** at which the reaction happens.

This week, we will focus on equilibrium, which describes the extent of a reaction. The extent of a reaction tells us the concentrations of reactants and products that exist an infinitely long time after the reaction began, or, when the reaction is **“done changing.”**

## 1. Equilibria



First of all, what even is the state of equilibrium? Equilibrium is *not* about rate - that is, it is *not* the point at which  $[reactants] = [products]$ .

Instead, equilibrium refers to the point at which the forward rate = reverse rate. This means that, once a reaction has reached equilibrium, there is no net change in  $[reactants]$  or  $[products]$ .

Recall that the rate of the reaction is given by the following:

$$rate = k[A]^a \leftarrow m$$

We can write the rates for both the forward and reverse reactions in this form, and generate:

$$rate_{fwd} = rate_{rev}$$
$$k_{fwd} [A]_{eq}^a = k_{rev} [B]_{eq}^b$$

$$\frac{k_{fwd}}{k_{rev}} = \frac{[B]_{eq}^b}{[A]_{eq}^a}$$

Based upon this ratio of  $k_{\text{fwd}} / k_{\text{rev}}$ , we can define a new constant,  $K$ , called the **equilibrium constant**:

$$K = \frac{k_{\text{fwd}}}{k_{\text{rev}}} = \frac{[B]_{\text{eq}}^b}{[A]_{\text{eq}}^a}$$

If  $K \gg 0$ , then the forward reaction is favored and very little reactant remains at equilibrium (the reaction “goes to completion”).

If  $K \approx 0$ , then neither the forward reaction nor the reverse reaction is favored, and large amounts of reactants and products exist at equilibrium.

If  $K \ll 0$ , then the reverse reaction is favored and a lot of reactant remains at equilibrium (“no reaction”).

## 2. The Reaction Quotient



We just talked about  $K$ , which we mathematically defined as the ratio of rate constants. What is  $Q$ ?

$Q$  is the reaction quotient, and it is defined as:

$$Q = \frac{[B]^b}{[A]^a}$$

$K$  is a constant, and therefore remains the same. Its job is to tell us which “side” of a reaction is favored by giving the ratio of the rates (and therefore the ratio of the concentrations of the products and reactants) of a reaction at equilibrium.  $Q$  is not a constant, however, and changes throughout the course of a reaction as the concentrations of products and reactants change.

Notice however, that  $K = Q$  when the reaction has reached equilibrium. If this is confusing, review the last two pages and notice that the math “checks out.”

If we are given the  $K$  or  $Q$  values for individual steps of a reaction, we can find the overall value by multiplying the values from individual steps together:

$$K_{\text{overall}} = K_1 \times K_2 \times \dots \times K_n$$
$$Q_{\text{overall}} = Q_1 \times Q_2 \times \dots \times Q_n$$

### 3. Comparing K and Q

Because K gives us a “snapshot” of what equilibrium looks like and Q tells us where we are at any point in the reaction’s progress, by examining both values we can determine if a reaction has reached equilibrium, and if not, we can determine which “direction” the reaction is proceeding (that is, towards the products or reactants).

There is a really easy trick to this. First, order K and Q, and leave some space in between the two letters. For this trick to work, we must arrange K before Q, and if you need help remembering this, think alphabetical order or use the mnemonic “King before Queen.”

K                  Q

Next, look at what your problem tells you. Is the K value less than or greater than the Q value at that specific point in time? Fill in the sign in the blank that you left.

less  
than

K                  <                  Q

greater  
than

K                  >                  Q

A                  →                  B

reactants

products

Finally, think about the sign not as less than or greater than, but instead as an arrow. We know that reactants are on the left side of a reaction and products are on the right side of a reaction.

If our “arrow” is pointing towards the left ( $K < Q$ ), then the reaction is moving towards the reactants.

If our “arrow” is pointing towards the right ( $K > Q$ ), then the reaction is moving towards the products.

Of course, if we have an equal sign, then we are at equilibrium and the reaction is not moving toward either side.

## 4. ICE Tables

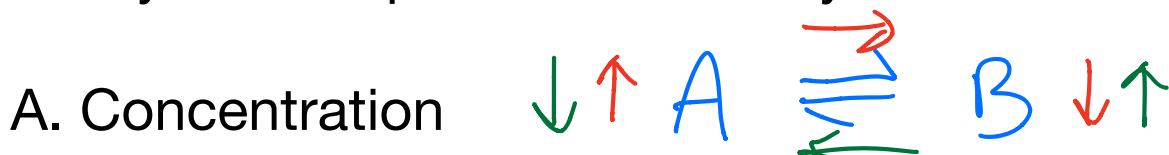
There are many kinds of scenarios you can expect to see when doing initial-change-equilibrium problems. It is important to note that these problems can deal either in pressures or concentrations. I've found that the following video nicely summarizes this topic:

<https://youtu.be/aJ0KNQ5-Kal>



## 5. Le Châtelier's Principle

The best way to think about this principle is to consider it as a “disturbance” to equilibrium. When we disturb the system by changing the concentration of reactant or product/ changing the pressure/ changing the temperature, how does the system respond? Which way does the reaction shift?



I think your textbook explains it clearly:

“If the concentration of A increases, the system reacts to consume some of it. If the concentration of B decreases, the system reacts to produce some of it.”

Therefore, an increase in reactants or a decrease in products will drive the reaction towards the products. A decrease in reactants or an increase in products will drive the reaction towards the reactants.

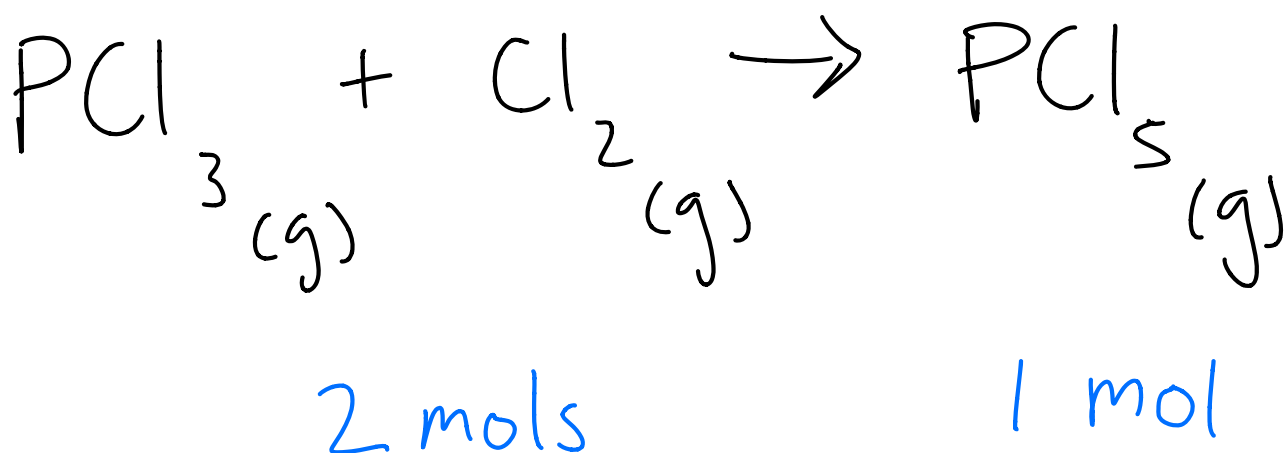
### B. Pressure/volume

Our equilibrium system can be disturbed by an increase in pressure (decrease in volume). The reaction naturally “de-escalates” by favoring the side of the reaction with the fewer number of moles.

Likewise, equilibrium can be disturbed by a decrease in pressure (increase in volume). In this case, the side of the reaction with more moles of gas is favored.

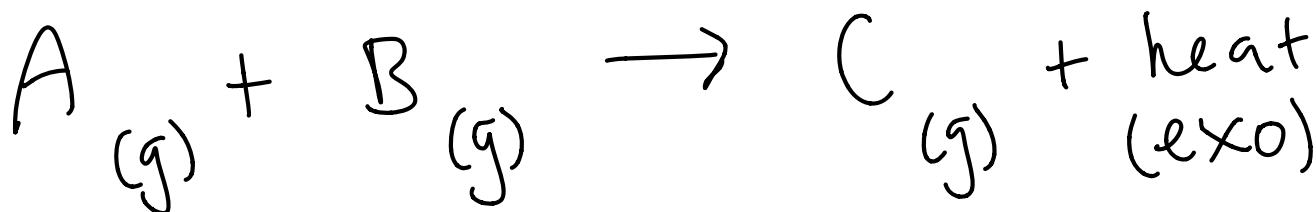
This seems abstract, so let's over-simplify it: if we increase the pressure, we decrease the volume of a container, and fewer moles of gas are required to fill the container. The reaction will therefore shift towards the side with fewer total moles of gas.

Textbook example:



C. Temperature

Consider the following reaction:



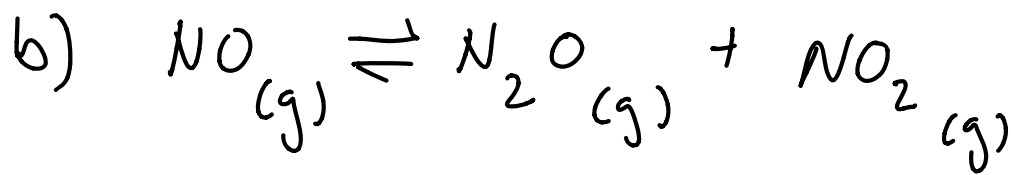
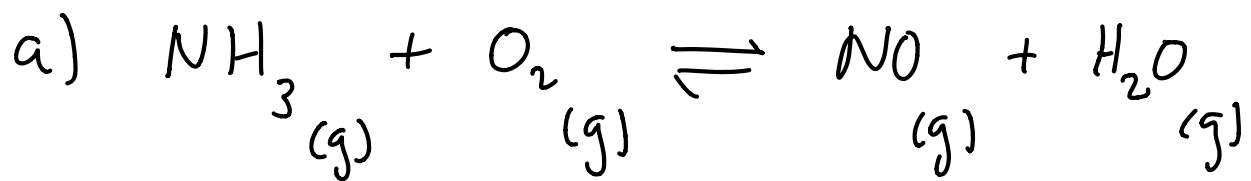
If we introduce heat into or remove heat from a system, the reaction will shift towards the side that can best “handle” this change in order to best minimize change. But what does that mean?

Recall that an endothermic reaction ( $\Delta H_{rxn}^{\circ} > 0$ ) absorbs heat. If we add heat to the system, the reaction will naturally shift towards the endothermic direction because the endothermic direction is able to absorb it (maintains the temperature as much as possible).

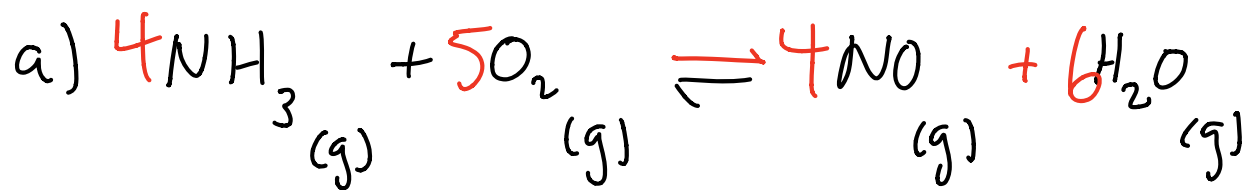
An exothermic reaction ( $\Delta H_{rxn}^{\circ} < 0$ ) releases heat. If we remove heat from the system, the reaction will naturally shift towards the exothermic direction because the exothermic direction will give off whatever heat exists (maintains the temperature as much as possible).

Problems:

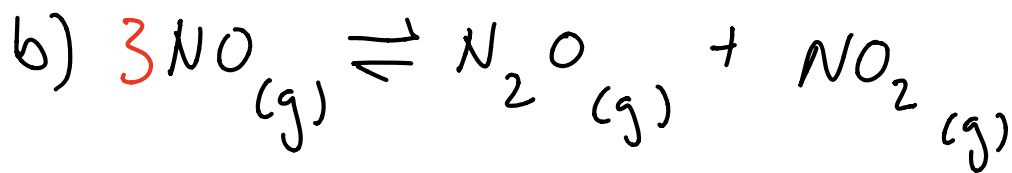
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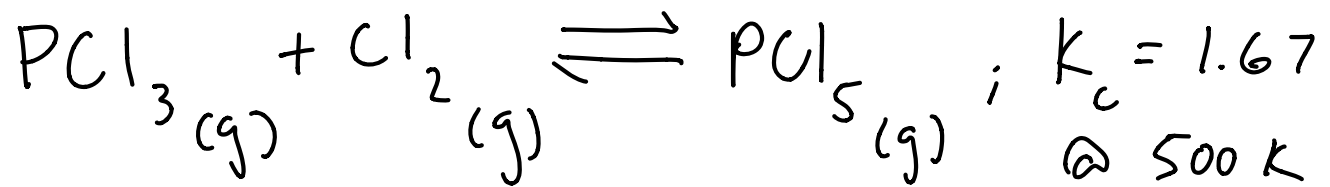


$$Q_c = \frac{[\text{NO}]^4 [\text{H}_2\text{O}]^6}{[\text{NH}_3]^4 [\text{O}_2]^5}$$

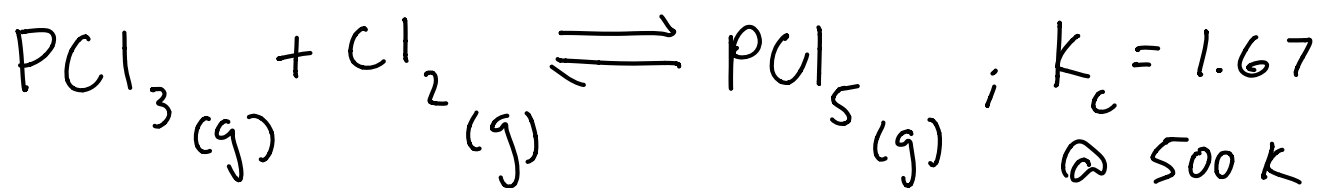


$$Q_c = \frac{[\text{NO}_2][\text{N}_2\text{O}]}{[\text{NO}]^3}$$

② Calculate  $K_p$  for the following reaction ( $K_p = K_c(RT)^{n(g)}$ ,  $R = 0.0821 \frac{\text{atm} \cdot \text{L}}{\text{mol} \cdot \text{K}}$ ):



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$$K_p = K_c (RT)^{-1}$$

$$= 1.67 (0.0821 \times 500)^{-1}$$

$$= 4.07 \times 10^{-2}$$

③

In the following reaction,

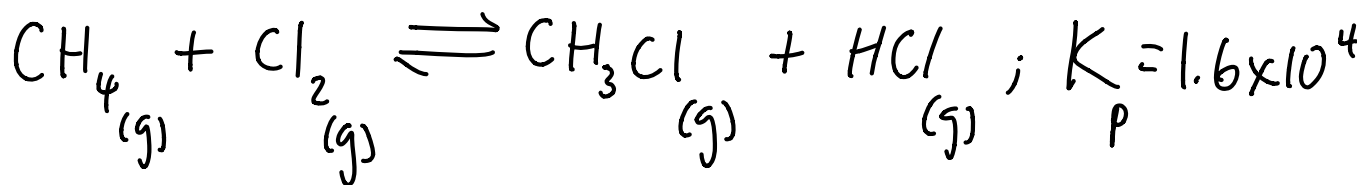
$$P_{\text{CH}_4} = 0.13 \text{ atm}, \quad P_{\text{Cl}_2} = 0.035 \text{ atm},$$

$$P_{\text{CH}_3\text{Cl}} = 0.24 \text{ atm}, \text{ and}$$

$$P_{\text{HCl}} = 0.47 \text{ atm. According to}$$

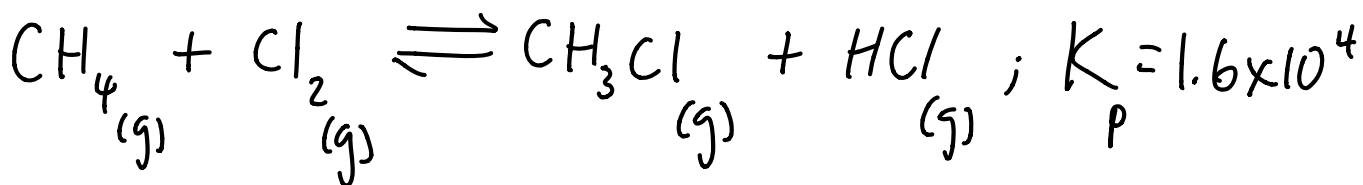
the reaction below, is

$\text{CH}_3\text{Cl}$  or  $\text{CH}_4$  forming?





③ In the following reaction,  
 $P_{\text{CH}_4} = 0.13 \text{ atm}$ ,  $P_{\text{Cl}_2} = 0.035 \text{ atm}$ ,  
 $P_{\text{CH}_3\text{Cl}} = 0.24 \text{ atm}$ , and  
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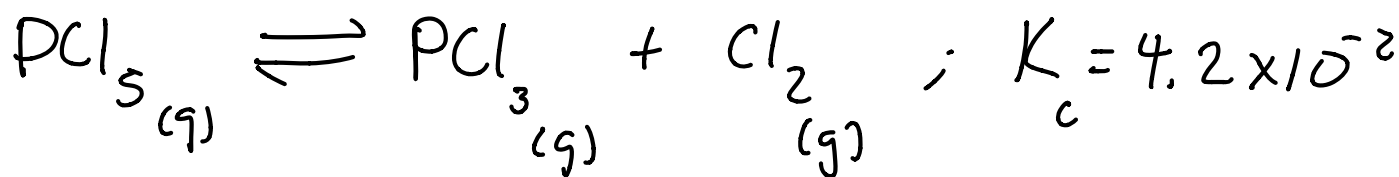


$$Q_P = \frac{(0.24)(0.47)}{(0.13)(0.035)} = 25$$

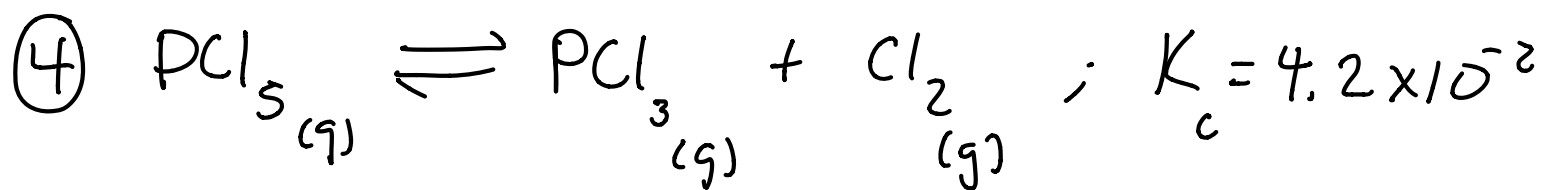
$K_P > Q_P$  (shift towards products)

$\text{CH}_3\text{Cl}$  is forming

④ Dr. Lopez mixes 0.1050 mol of  $\text{PCl}_5$  with 0.0450 mol of  $\text{Cl}_2$  and 0.0450 mol of  $\text{PCl}_3$  in a 0.5 L flask at  $250^\circ\text{C}$ , according to the following reaction:



If  $[\text{PCl}_5] = 0.2065 \text{ M}$  at equilibrium, what are the equilibrium concentrations of the other components?



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	$\text{PCl}_5$	$\text{PCl}_3$	$\text{Cl}_2$
I	0.2100	0.090	0.090
C	-x	+x	+x
E	0.21-x	0.09+x	0.09+x

$$0.21 - x = 0.2065$$

$$0.21 - 0.2065 = x$$

$$x = 0.0035 \text{ M}$$

$$\begin{aligned} [\text{PCl}_3] &= [\text{Cl}_2] = 0.09 + 0.0035 \\ &= 0.0935 \text{ M} \end{aligned}$$