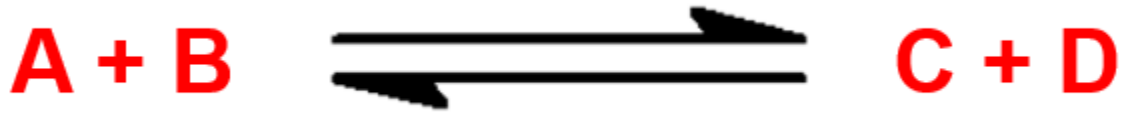
Chemical Equilibrium

(Dynamic Equilibrium and Equilibrium Constants)

What is Dynamic Equilibrium?

Until now, we've talked mostly about reactions with one-way arrows, like this:

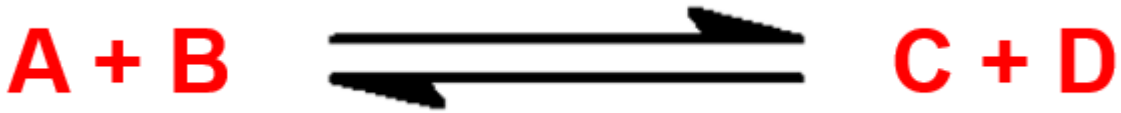
In this chapter we'll discuss reactions that have two-way arrows, like this:



Such reactions are called ***equilibrium reactions***.

What is Dynamic Equilibrium?

Dynamic equilibrium does NOT necessarily mean that the amounts of reactants and products are equal.



Instead, ***dynamic equilibrium*** just means that the speed at which reactants are converting to products is equal to the speed at which products are converting back to reactants.

In other words, being at ***equilibrium*** means that the speed or rate is the same, going from right-to-left, as it is going from left-to-right. It also does NOT mean that the reaction has stopped. Once equilibrium is reached, *concentrations* stop changing, which makes the reaction *appear* to be stopped.

Rate Law Review

In a prior chapter, we learned that for any generic reaction:

$$aA + bB \rightarrow cC + dD$$

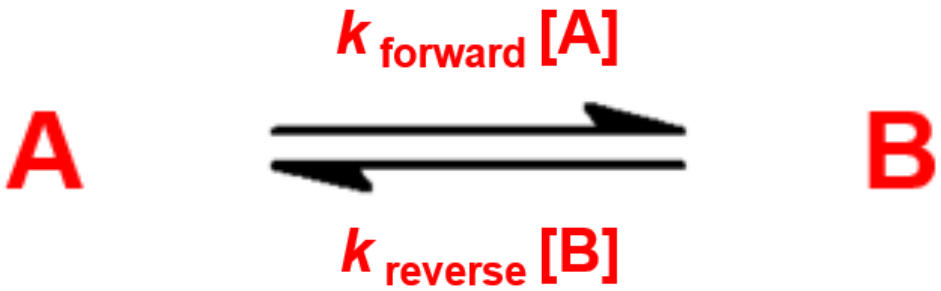
. . . Its ***rate law*** is:

$$\text{Rate} = k[A]^m[B]^n$$

We also learned that the products do NOT appear in the ***rate law***. Furthermore, if the above reaction is an ***overall reaction***, then **m** and **n** *have to be determined experimentally* and are not necessarily equal to coefficients **a** and **b**. If the above reaction is an ***elementary reaction***, then **m** and **n** *are* equal to **a** and **b**.

Equilibrium Constants

However, a reaction at ***equilibrium*** . . .



. . . is actually *two* reactions occurring simultaneously at the same rate: the forward reaction (**A** → **B**) and the reverse reaction (**B** → **A**). Because these two reactions are occurring simultaneously and at the same rate, we can say:

$$\text{Rate} = k_{forward}[A] = k_{reverse}[B]$$

Equilibrium Constants

$$\text{Rate} = k_{\text{forward}}[\text{A}] = k_{\text{reverse}}[\text{B}]$$

This means algebraically that:

$$\text{Rate} = \frac{k_{\text{forward}}}{k_{\text{reverse}}} = \frac{[\text{B}]}{[\text{A}]} = \text{a constant}$$

Equilibrium Constants

$$\text{Rate} = k_{\text{forward}}[A] = k_{\text{reverse}}[B]$$

This means algebraically that:

$$\text{Rate} = \frac{k_{\text{forward}}}{k_{\text{reverse}}} = \frac{[B]}{[A]} = K_C$$

Hence, the overall ***rate constant*** (K_C) for our reaction is:

$$K_C = \frac{[B]}{[A]}$$

Equilibrium Constants

Thus, unlike one-way reactions, ***equilibrium reactions'*** rate constants DO depend *only* on the reaction's coefficients and not on the reaction's mechanism. So, for any generic reaction at ***equilibrium:***

. . . . The ***equilibrium rate constant*** (K_c) is:

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

Equilibrium Constants

Thus, unlike one-way reactions, ***equilibrium reactions'*** rate constants DO depend *only* on the reaction's coefficients and not on the reaction's mechanism. So, for any generic reaction at ***equilibrium:***

. . . . The ***equilibrium rate constant*** (K_c) is:

$$K_c = \frac{\text{products}}{\text{reactants}}$$

K_c Details

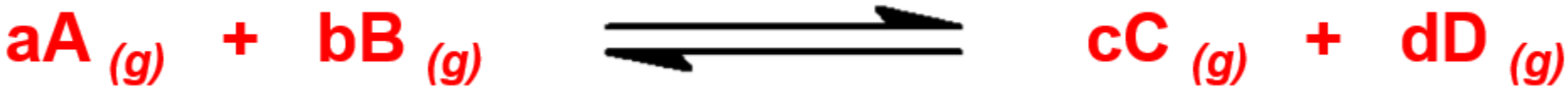
A few things to remember:

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

- For reasons that you don't have to understand, K_c has no units.
- Solids and liquids do NOT appear in the K_c expression. Thus, if your ***equilibrium reaction*** includes substances with ***(s)*** or ***(l)*** terms to indicate that they are solids or liquids, you should leave these substances out of your K_c expression.
- K_c is an equilibrium constant in terms of ***concentration*** (that's why we use the "***c***" in K_c). **[A]**, **[B]**, **[C]**, and **[D]** are concentrations in ***molarity*** (moles solute/liters of solution).
- Only temperature can change the equilibrium constant ***K***.

K_P

For equilibrium reactions involving gases, we can produce ***equilibrium expressions*** in terms of pressure, instead of concentration. We call these expressions K_P. Thus, for any generic equilibrium reaction:



. . . The ***equilibrium constant expression*** in terms of pressure is:

$$K_P = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

K_C and K_P do not have to equal each other. They measure different things. One is in terms of concentration (***molarity***) and the other in terms of ***pressure***.

Sometimes we use K_P because it's easier to measure the partial pressure of a gas than its concentration.

Only ***temperature*** can change the ***equilibrium constant*** ***K*** (either K_C or K_P)!

Questions

For the following ***dynamic equilibrium:***

$$N_{2\,(g)} + 3\,H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

1. What is the ***rate constant expression*** in terms of concentration, K_C?
2. What is the ***rate constant expression*** in terms of pressure, K_P?
3. If $K_C = 10$, then what is K_C for the reverse reaction,
   $2NH_3 \rightleftharpoons N_{2\,(g)} + 3\,H_2$?

Henry Louis Le Chatelier

Chemical Equilibrium

(Equilibrium Balance and Reaction Quotients)

Reviewing Equilibrium Constants

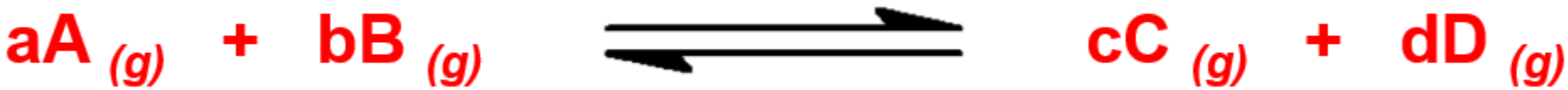
In our last video, I taught you that for the following generic reaction at ***equilibrium:***

. . . . The ***equilibrium rate constant*** in terms of *concentration* (K_c) is:

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

Reviewing Equilibrium Constants

I also taught you that for ***equilibrium reactions*** involving gases, we can produce ***equilibrium expressions*** in terms of pressure (instead of concentration), which are called K_P. For any such generic reaction at ***equilibrium***:

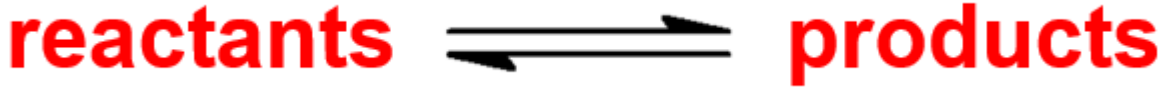


. . . The ***equilibrium constant expression*** in terms of *pressure* is:

$$K_P = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

What Does *K* Tell Us?

Whether we're discussing K_C or K_P, you can hopefully see that in general, *K* looks like this:



$$K = \frac{\text{products}}{\text{reactants}}$$

What does *K* actually tell us?

K	Meaning
$K > 1$	***products*** are favored at equilibrium
$K < 1$	***reactants*** are favored at equilibrium

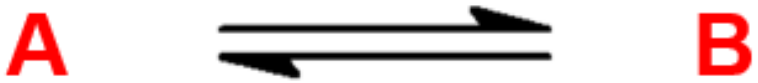
What If It's Not at Equilibrium Yet?

Everything we've talked about so far in this chapter is based on the idea that our reactions have already reached ***equilibrium***. But what if we have an ***equilibrium reaction*** that is progressing *toward* equilibrium, but just hasn't gotten there yet? What happens then?

In this case, you can still measure the amounts of products and reactants and put those numbers into your ***K*** expression. If that ends up giving you your known ***K*** value, then your reaction has reached ***equilibrium***. If not, then it has not yet reached equilibrium and needs to keep going.

What If It's Not at Equilibrium Yet?

For example, imagine that the following ***equilibrium reaction***:



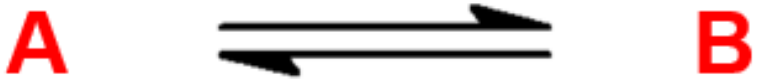
. . . Has a known K_c value of **7**.

Now imagine that while running this reaction, you measure **[A]** and **[B]** and find that **[A] = 3 M**, and **[B] = 18 M**.

Is the reaction at ***equilibrium*** yet? How would you figure that out?

What If It's Not at Equilibrium Yet?

This reaction's ***equilibrium constant expression:***



. . . Is:

$$K_C = \frac{[B]}{[A]}$$

What If It's Not at Equilibrium Yet?

Remember that you measured the following:

[A] = 3 M, [B] = 18 M

$$K_c = \frac{[B]}{[A]}$$

We were also told that this particular reaction has a known K_c value of **7**.

So, if your reaction is at ***equilibrium***, then if you put *these* values into their respective locations in your K_c expression, it should give you an answer of **7**.

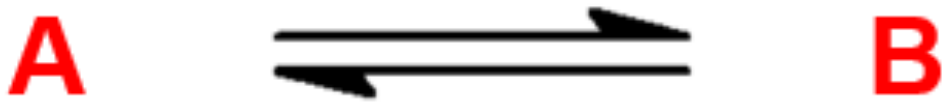
What If It's Not at Equilibrium Yet?

The "K_C" of your system in its current state, then, is:

$$\text{“}K_C\text{”} = \frac{[B]}{[A]} = \frac{18\ M}{3\ M} = 6$$

Is your system at ***equilibrium?*** No! It's not at ***equilibrium*** until your "K_C" value reaches **7**.

What If It's Not at Equilibrium Yet?



$$K_C = \frac{[B]}{[A]}$$

At ***equilibrium***, K_C = **7**. Your "K_C" is currently **6**. In which direction (to the right or the left) does your reaction need to shift?

"K_c" is Actually Called "Q_c"

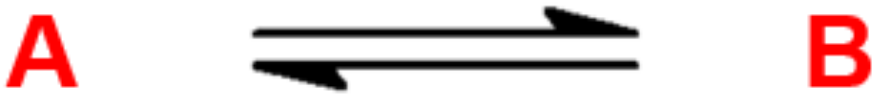
This "K_c" value is actually called the ***reaction quotient***, or Q_c.

Q_c is what you get when you measure the amounts of products and reactants in an ***equilibrium reaction*** and then insert those numbers into your K_c expression. And yes, you can have K_P and Q_P, as well.

Once again, when doing this, it *is* possible that your reaction has not yet reached ***equilibrium***. When that is the case, then $Q \neq K$.

Remember, then, that Q is pretty much the same as K, except that Q may or may not be at ***equilibrium*** yet.

What Does *Q* Tell Us?



$$K_c = \frac{[B]}{[A]}$$

$$Q_c = \frac{[B_{\text{may or may not be at equilibium yet}}]}{[A_{\text{may or may not be at equilibium yet}}]}$$

What Does *Q* Tell Us?

$$Q_c = \frac{[B]}{[A]}$$

What does *Q* actually tell us?

Q	Meaning
$Q > K$	Not at equilibrium. *Q* is too big. Too much product. Rxn needs to shift left.
$Q < K$	Not at equilibrium. *Q* is too small. Too much reactant. Rxn needs to shift right.
$Q = K$	At equilibrium.

Questions

At 1000 K, the following reaction:

$$2\ SO_{2\ (g)} + O_{2\ (g)} \rightleftharpoons 2\ SO_{3\ (g)}$$

. . . Has a K_c value of 2.8×10^2.

- Which side of the reaction is favored at equilibrium under these conditions?
- Is the following mixture of SO_2, O_2, and SO_3 at 1000 K at equilibrium?

$$[SO_3] = 230\ M;\ [O_2] = 6\ M,\ [SO_2] = 3\ M$$

- If not, which direction does it need to move to achieve equilibrium?

Henry Louis Le Chatelier

Chemical Equilibrium

(Le Chatelier's Principle)

Le Châtelier's Principle

Le Châtelier's Principle states that "if a system at equilibrium is disturbed, then it will shift in whichever direction it has to, to restore equilibrium."

For the EXAM, you will need to know how systems at ***equilibrium*** are affected by the each of the following four kinds of "disturbances":

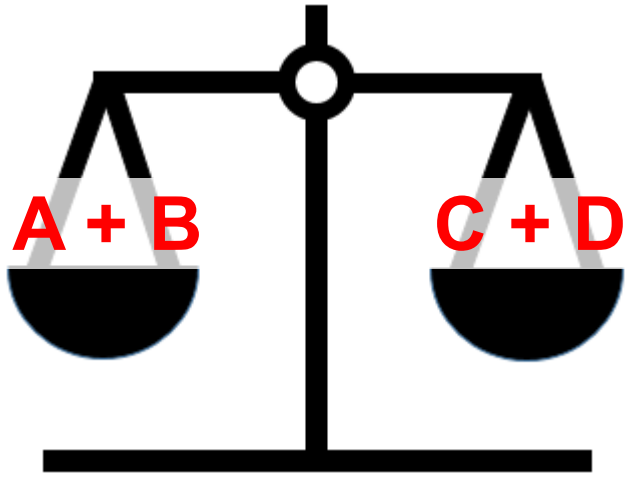
- Adding or removing reactants or products
- Changing temperature
- Changing volume or pressure
- Adding a catalyst

Adding or Removing Reactants or Products

Imagine we have the following reaction:

$$A + B \rightleftharpoons C + D$$

. . . in perfect ***equilibrium***. As you know, for systems at ***equilibrium***, the rate of the forward and reverse reactions is the same. In that sense, the reaction is balanced, kind of like this:



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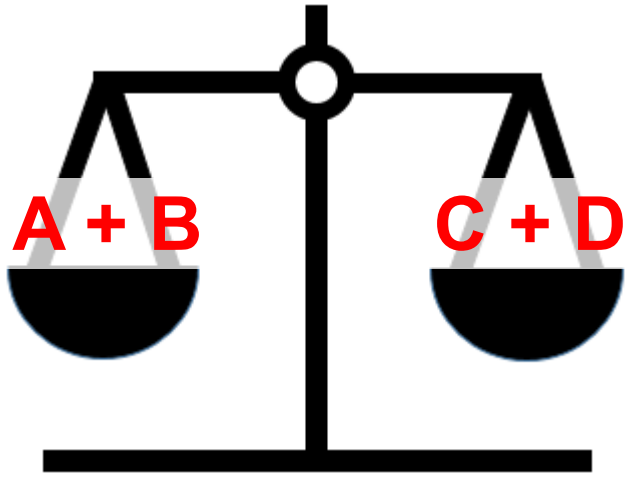

Before going on, I want to stress that being at ***equilibrium*** does NOT mean that the *AMOUNTS* of reactants and products on both sides of the equation are equal. It just means that the *RATES* of the forward and reverse reactions are equal. Thus, using a scale-balance as a metaphor can be misleading. Again, it does NOT mean that we have equal amounts on both sides of the equation. However, the scale-balance metaphor is helpful for understanding ***Le Châtelier's principle***.

Adding or Removing Reactants or Products

Imagine we have the following reaction:

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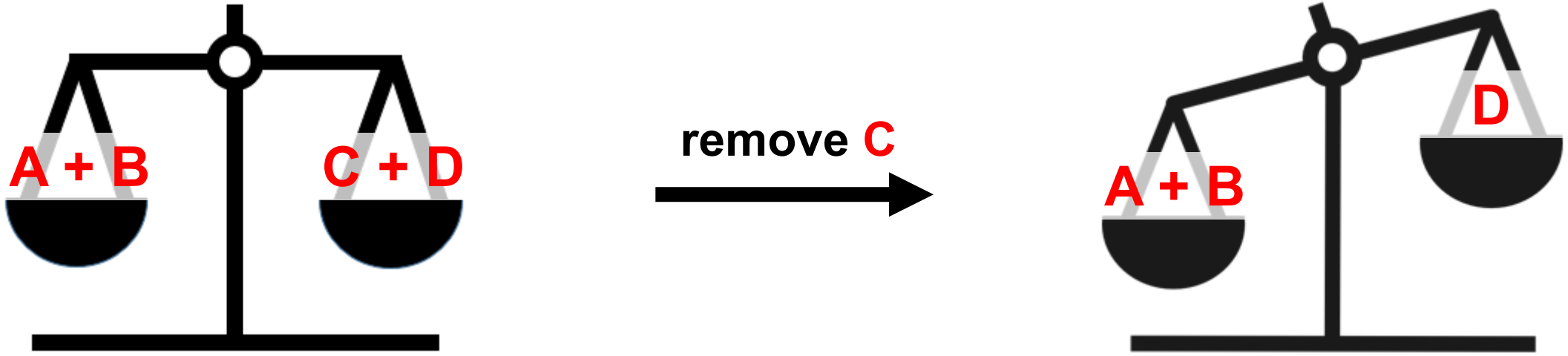
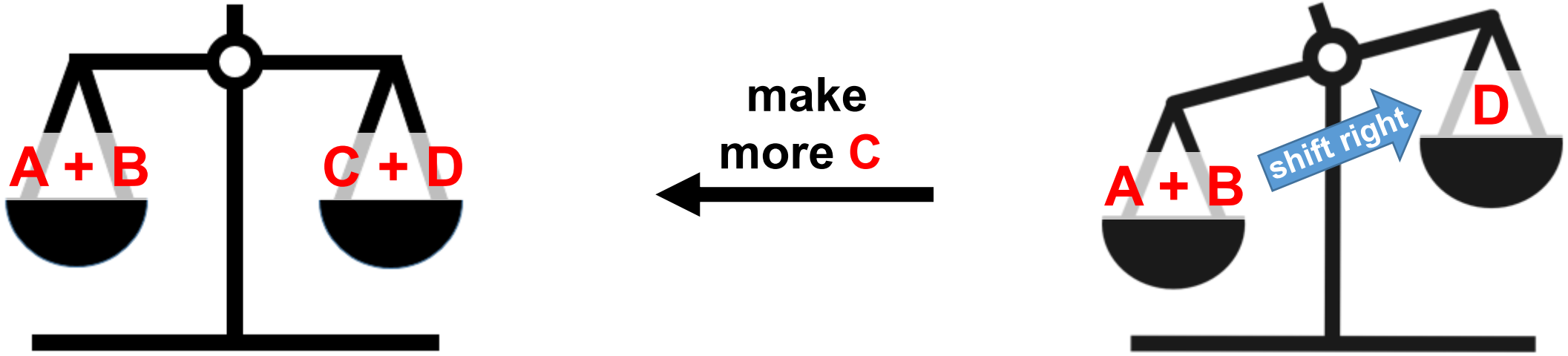


Adding or Removing Reactants or Products

So in this reaction, which we "disturbed" by removing **C**, how could balance be restored?

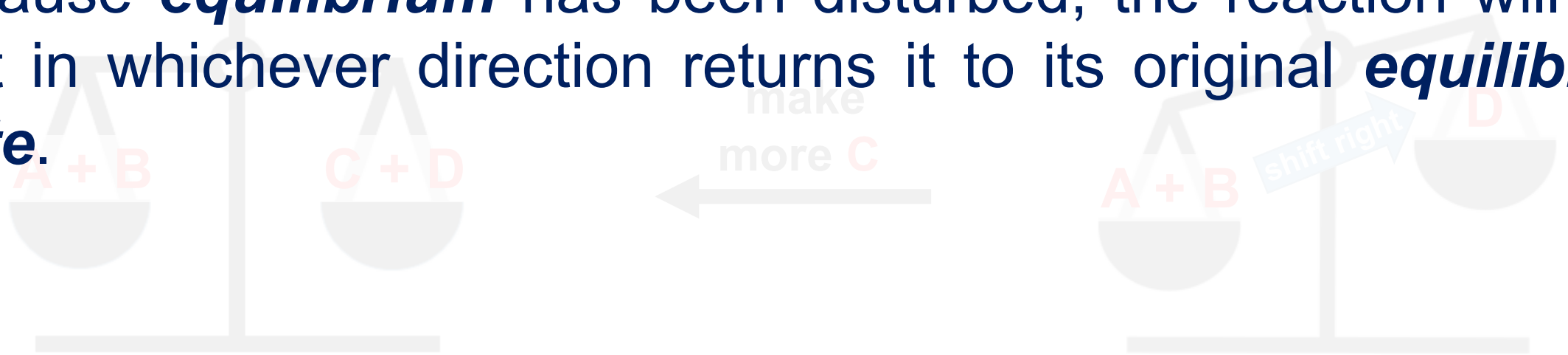
If **A** and **B** shifted to the right to *make* more **C**, then balance (***equilibrium***) would be restored.



Adding or Removing Reactants or Products

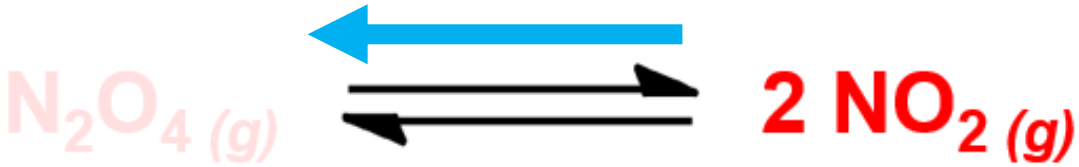
This is how ***Le Châtelier's Principle*** applies when the amount of reactants or products in an ***equilibrium reaction*** are changed.

Because ***equilibrium*** has been disturbed, the reaction will now shift in whichever direction returns it to its original ***equilibrium state***.



Questions

Consider the following ***equilibrium reaction:***



In which direction will the reaction shift to restore ***equilibrium*** if:

- N_2O_4 is removed? **shift left**
- NO_2 is removed?
- N_2O_4 is added?
- NO_2 is added?

Questions

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Questions

Consider the following ***equilibrium reaction:***

In which direction will the reaction shift to restore ***equilibrium*** if:

- **N_2O_4** is removed? **shift left**
- **NO_2** is removed? **shift right**
- **N_2O_4** is added? **shift right**
- **NO_2** is added? **shift left**

Changing Temperature

If a reaction is ***exothermic*** (***ΔH*** is negative), then the reaction *gives off heat*. When this happens, we can just treat **heat** like a product. For example:

$$H_{2\,(g)} + F_{2\,(g)} \rightleftharpoons 2\,HF_{(g)}$$

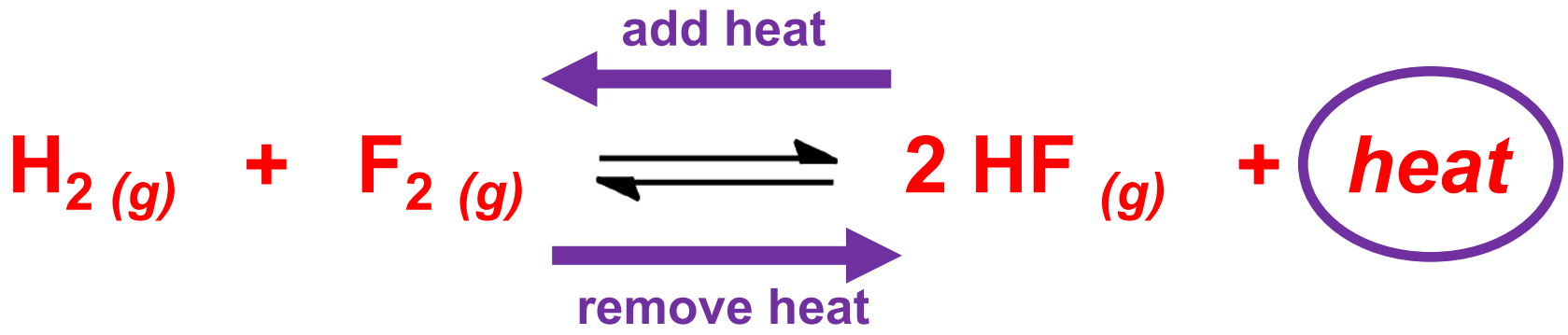
$$\Delta H = -573.2\ kJ$$

exothermic
(gives off heat)

In which direction will the reaction shift to restore equilibrium, if we remove or add heat?

Changing Temperature

If a reaction is ***exothermic*** (***ΔH*** is negative), then the reaction *gives off heat*. When this happens, we can just treat **heat** like a product. For example:



In which direction will the reaction shift to restore equilibrium, if we remove or add heat? We now treat heat like a product. If we *increase* temperature, then we **add heat**, which shifts the reaction to the left. If we *decrease* temperature, then we **remove heat** (reaction shifts right).

Changing Temperature

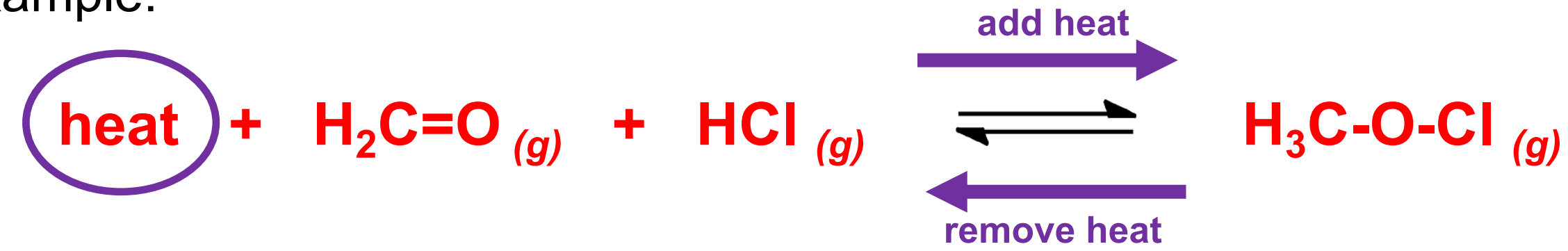
If a reaction is ***endothermic*** (***ΔH*** is positive), then the reaction *consumes heat*. When this happens, we can just treat **heat** like a reactant. For example:

endothermic (consumes heat)

In which direction will the reaction shift to restore equilibrium, if we remove or add heat?

Changing Temperature

If a reaction is ***endothermic*** (***ΔH*** is positive), then the reaction *consumes heat*. When this happens, we can just treat **heat** like a reactant. For example:



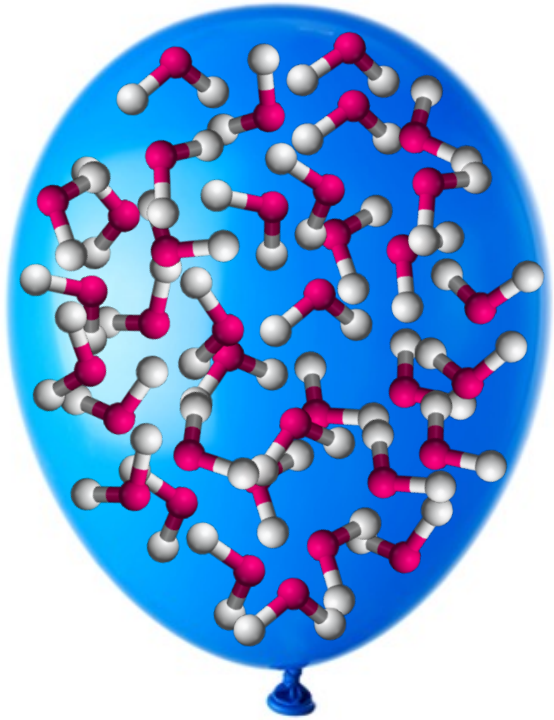
In which direction will the reaction shift to restore equilibrium, if we remove or add heat? We now treat heat like a reactant. If we *increase* temperature, then we **add heat**, which shifts the reaction to the right. If we *decrease* temperature, then we **remove heat** (reaction shifts left).

Changing Volume or Pressure

When pressure is increased, ***equilibrium reactions*** shift in whichever direction reduces the number of gas molecules.

Why?

I like to imagine the system being like a crowded room, where the number of gas molecules, ***n***, is like the number of people in the room. If we increase ***n*** (the number of people in the room), does the pressure the people feel go up or down? Up, of course.



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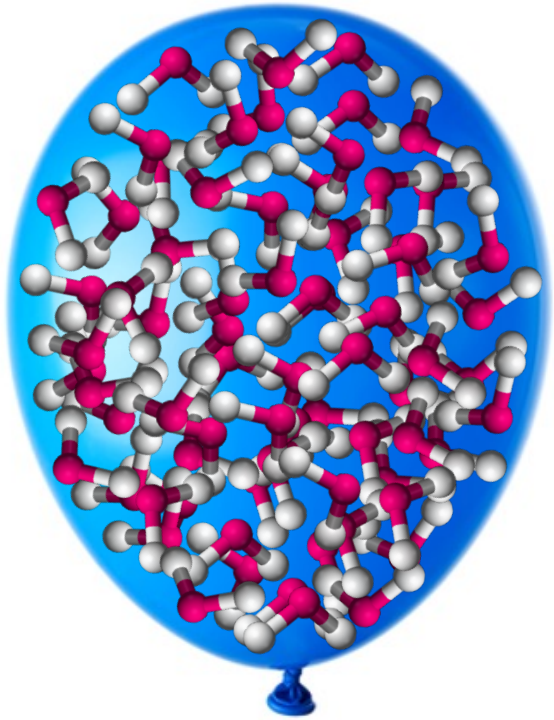
How can that pressure be relieved? By removing people (gas molecules). To do that, the reaction shifts to whichever side has fewer gas molecules.

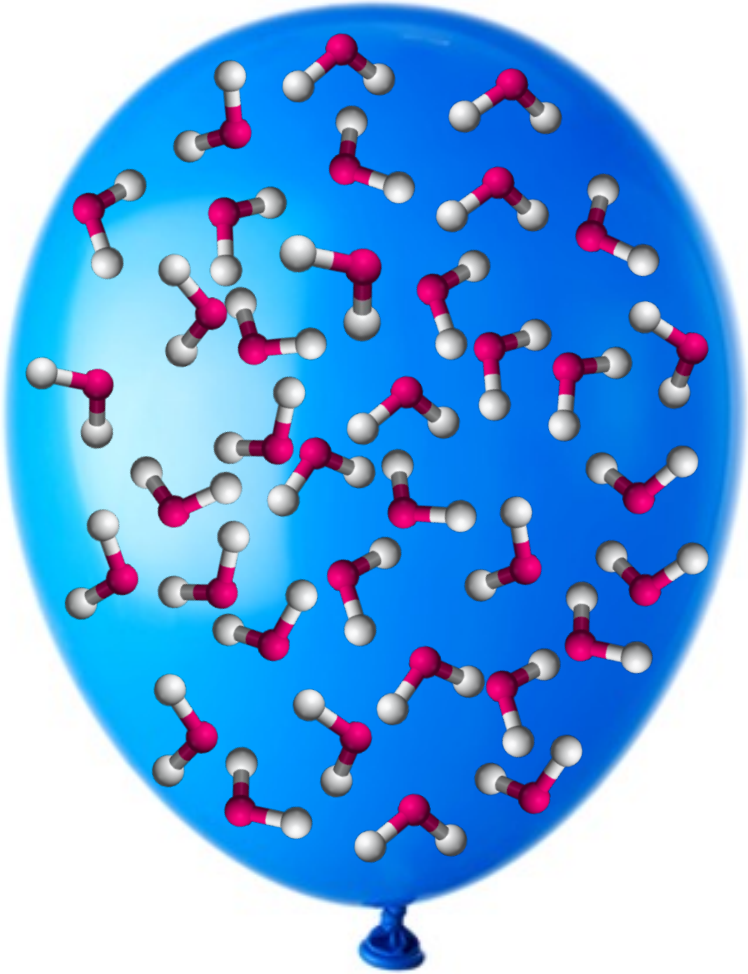


Changing Volume or Pressure

Volume and pressure are inversely related. As volume decreases, pressure increases, and vice versa. Thus, when volume is decreased, pressure goes up, and ***equilibrium reacions*** shift in whichever direction reduces the number of gas molecules.

Why?

If volume (the size of the room) decreases, does the pressure the people feel go up or down? Up, of course.



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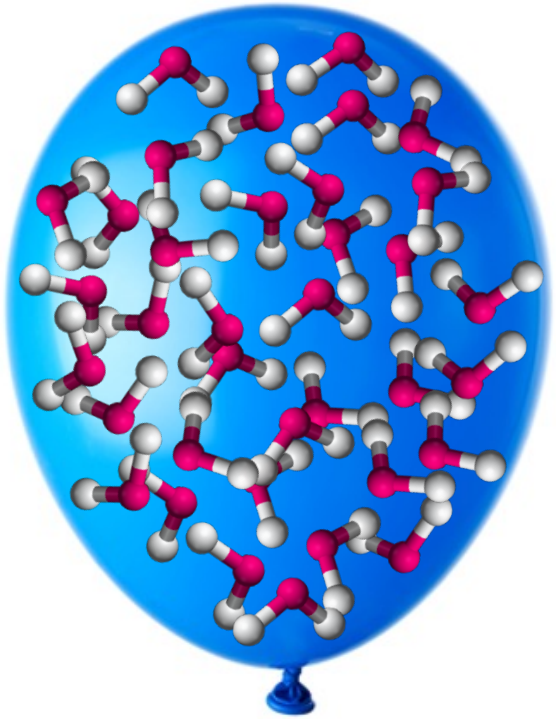
Why?

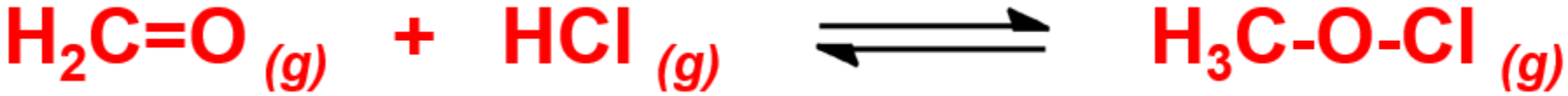
If volume (the size of the room) decreases, does the pressure the people feel go up or down? Up, of course!

↓V ≈ ↑P ≈ *reactions* shift to whichever side has fewer gas molecules



Changing Volume or Pressure

For the following equilibrium reaction:



. . . In which direction will the equilibrium shift when:

Inert gases do not effect equilibrium.

- The pressure is increased by adding $N_{2\,(g)}$? **no shift**
- The volume is increased? **shift left**
- The volume is decreased? **shift right**
- The pressure is decreased? **shift left**

Adding a Catalyst

As I've discussed in an earlier chapter, ***catalysts*** speed up reactions by providing an alternative pathway (an alternative ***mechanism***) with a lower ***activation energy*** (E_a) than the uncatalyzed pathway.

Catalysts do NOT shift ***equilibrium reactions*** in either direction, either to the right or the left. They make the reactions reach ***equilibrium*** more quickly. Hence, catalysts don't disturb ***equilibrium*** at all.

Questions

True or False: Adding a catalyst will shift the following equilibrium reaction to the right, increasing product yield:

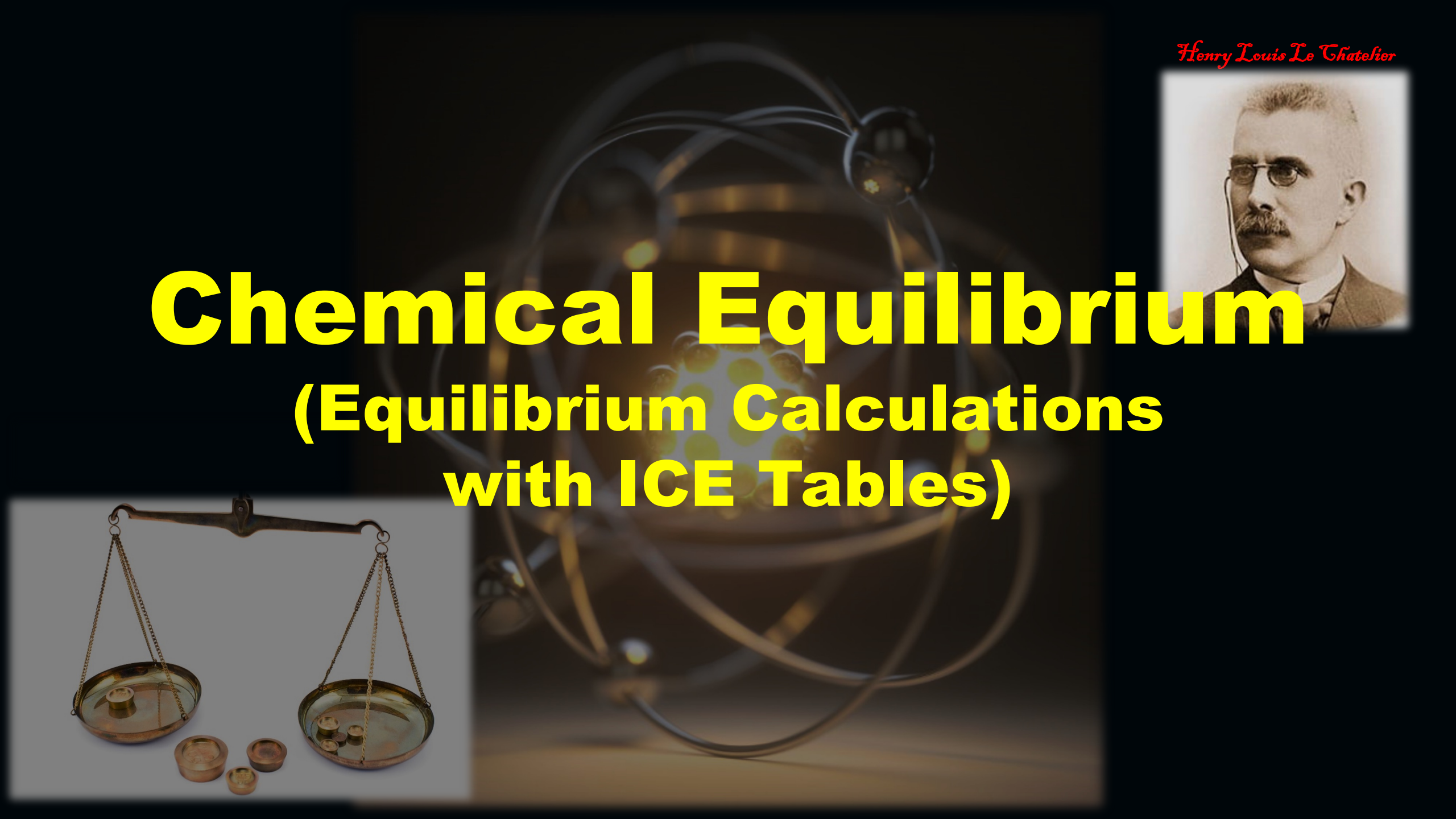
Final Questions

For the following equilibrium reaction:

$$C_{(s)} + 2\,H_{2\,(g)} \rightleftharpoons CH_{4\,(g)} \quad \Delta H = -75.0\ kJ$$

. . . In which direction will the equilibrium shift when:

- The temperature is increased?
- The temperature is decreased?
- Pressure is increased by adding an inert gas?
- Volume is increased?
- A catalyst is added?



Chemical Equilibrium

(Equilibrium Calculations with ICE Tables)

Strong Electrolytes

When ***strong electrolytes*** (***strong acids***, ***strong bases***, or ***ionic compounds*** that readily dissolve in water, according to the ***solubility rules*** we covered in an earlier chapter) dissolve, the reaction arrows are more-or-less one-way:

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

$$KOH_{(aq)} \rightarrow K^+_{(aq)} + OH^-_{(aq)}$$

$$Ca(NO_3)_{2\,(aq)} \rightarrow Ca^{2+}_{(aq)} + 2\,NO_3^-{}_{(aq)}$$

In other words, they do NOT form ***equilibrium reactions***.

Strong Electrolytes

Calculations with ***strong electrolytes*** are pretty easy. Because they dissolve nearly completely, their arrows are one-way, which means that the number of moles of dissolved ions is calculated directly from the balanced equation:

$$HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$$

$$KOH_{(aq)} \rightarrow K^+_{(aq)} + OH^-_{(aq)}$$

$$Ca(NO_3)_{2\,(aq)} \rightarrow Ca^{2+}_{(aq)} + 2\,NO_3^-{}_{(aq)}$$

Weak Electrolytes

In contrast, ***weak electrolytes*** (***weak acids***, ***weak bases***, or ***ionic compounds*** that do NOT dissolve fully in water) have two-way ***equilibrium-reaction*** arrows, like this:

$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$

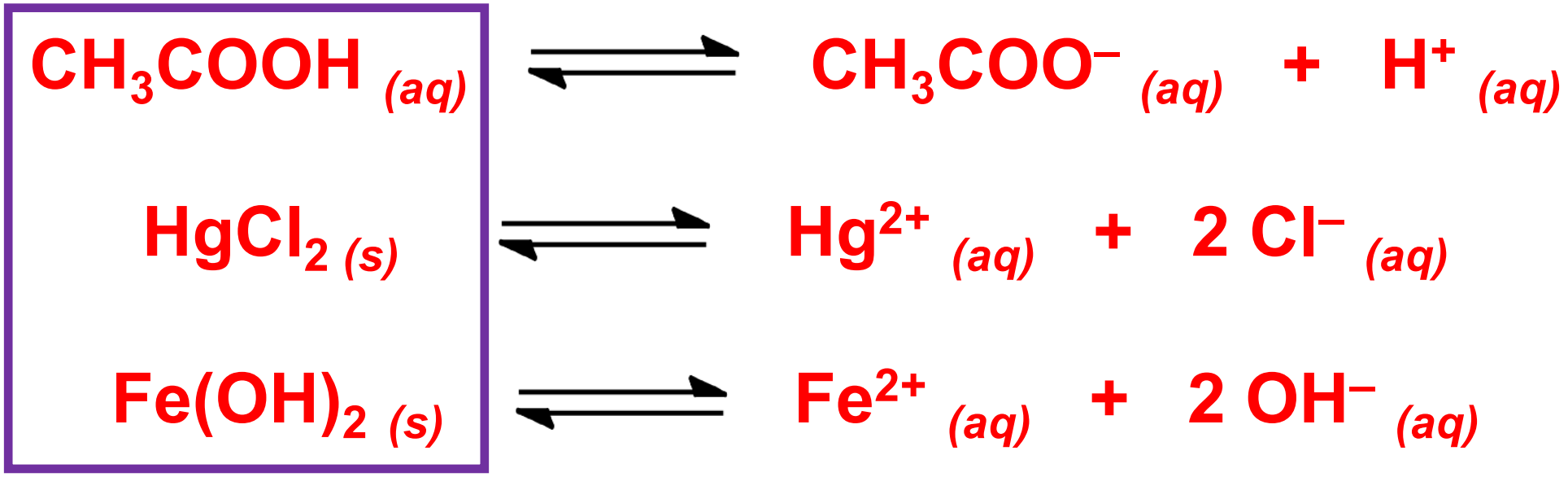
$HgCl_{2\,(s)} \rightleftharpoons Hg^{2+}_{(aq)} + 2\,Cl^-_{(aq)}$

$Fe(OH)_{2\,(s)} \rightleftharpoons Fe^{2+}_{(aq)} + 2\,OH^-_{(aq)}$

heavily favored

Weak Electrolytes

Calculations with these substances are a little more challenging because they only dissolve partially.



Weak *K* Values

Just like any other system in ***equilibrium***, weak electrolytes also have ***K*** values. For weak acids, we call their ***K*** values K_A's. For weak bases, their ***K*** values are called K_B's. For insoluble solids like $Fe(OH)_2$, which dissociate only limitedly in water, we called their ***K*** values K_{SP}'s (***sp*** stands for "solubility product"). Water also has its <u>*own*</u> ***K*** value, called K_W.

For all the different ***K*** values, however, the way you set up the ***K expression*** is pretty much the same as always.

Weak *K* Values

In other words, for any generic reaction at ***equilibrium***:

. . . . The ***equilibrium rate constant*** ($K_{whatever}$) is:

$$K_{whatever} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \approx \frac{[products]}{[reactants]}$$

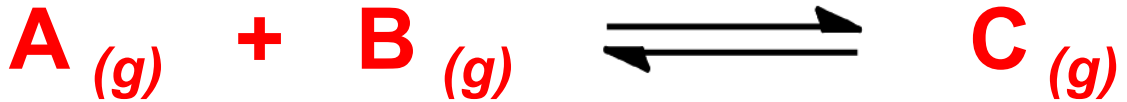
Weak *K* Values

Once again, calculations with ***weak electrolytes*** are a little less straightforward because they do not dissolve completely. For such calculations, we use a tool called ***ICE tables***.

"ICE," by the way, stands for Initial, Change, Equilibrium.

Questions

For the following ***equilibrium*** reaction:



. . . $K_C = 2.0 \times 10^{-3}$. If you start this reaction with the following initial concentrations:

[A] = 2.0 M, [B] = 0.5 M

. . . What are the concentrations of **A**, **B**, and **C** once the reaction reaches ***equilibrium?***

Questions

For the following ***equilibrium*** reaction:

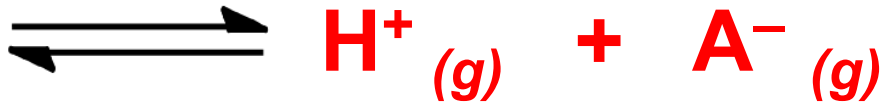
. . . $K_C = 5.0 \times 10^{-4}$. If you start this reaction with the following initial concentrations:

[A] = 1.0 M, [B] = 1.0 M

. . . What are the concentrations of **A**, **B**, and **C** once the reaction reaches ***equilibrium?***

Questions

For the following ***equilibrium*** reaction:



. . . $K_C = 4.0 \times 10^{-5}$. If you start this reaction with the following initial concentration:

[HA] = 0.1 M

. . . What is the ***equilibrium concentration*** of H^+?

Questions

Exactly 4.5 moles of N_2 and 2.5 moles of H_2 were added to a closed 1 L container at 278 K and allowed to react to form ammonia gas, NH_3. At equilibrium, there is 1 mole of NH_3. What is the equilibrium constant for this reaction at this temperature?

A. 1.4×10^{-2}
B. 2.78×10^{-2}
C. 3.56×10^{-2}
D. 8.47×10^{-2}
E. 2.5×10^{-1}

Henry Louis Le Chatelier

Chemical Equilibrium

(K_{sp})

Weak *K* Values

As I taught you previously, weak electrolytes in ***equilibrium*** *do* have ***K*** values, just like any other ***equilibrium*** system. Weak acids' ***K*** values are called K_A's. Weak bases' ***K*** values are called K_B's. Water's ***K*** value is called K_W. For insoluble solids like $Fe(OH)_2$, which dissociate (dissolve) only limitedly in water, their ***K*** values are called K_{SP}'s (***sp*** stands for "solubility product").

Weak *K* Values

For all these different ***K*** values, however, the way that you set up the ***K expression*** is pretty much the same as always. In other words, for any generic reaction at ***equilibrium***:

. . . . The ***equilibrium rate constant*** ($K_{whatever}$) is:

$$K_{whatever} = \frac{[C]^c[D]^d}{[A]^a[B]^b} \approx \frac{[products]}{[reactants]}$$

Weak K Values

In this video we'll do a bunch of calculations involving K_{sp}. The way you solve K_{sp} problems is:

- Write out the balanced chemical equation
- Write out the equilibrium expression, K_{sp}
- Solve for whatever is missing

On the EXAM, there are four general kinds of K_{sp} calculation questions:

- Calculate ***molar solubility***
- Calculate K_{sp}
- Calculate solubility for a ***common ion effect*** questions
- Determine if precipitation will occur

I'll now show you examples in each of these categories.

Calculating Molar Solubility

- What is the molar solubility of **$PbCl_2$**, whose ***K_{sp}*** is **2.5×10^{-4}**?

Calculating K_{sp}

- When dissolved in water at a certain temperature, a certain ionic compound **A_2B** is found to have a solubility of **2×10^{-6} M**. What is the K_{sp} of this compound?

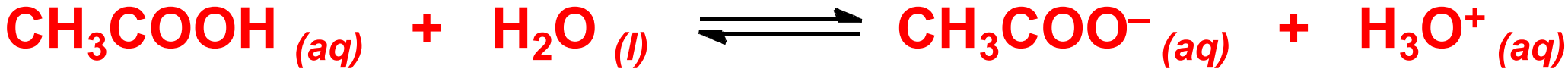
Henry Louis Le Chatelier

Chemical Equilibrium

(K_{sp})

Common Ion Effect

What would happen if we had this reaction:

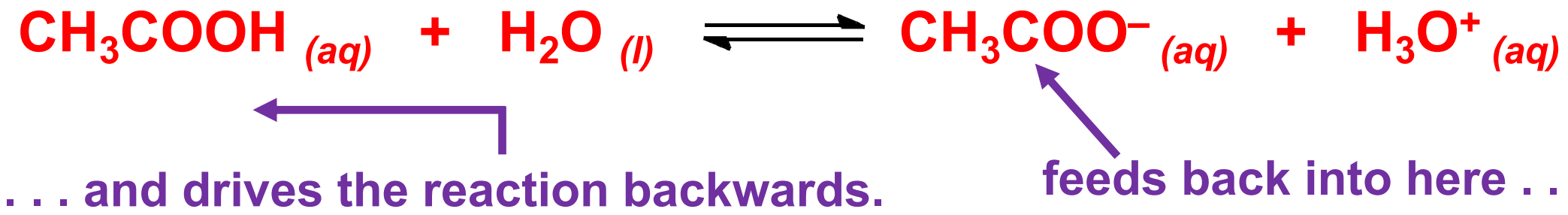


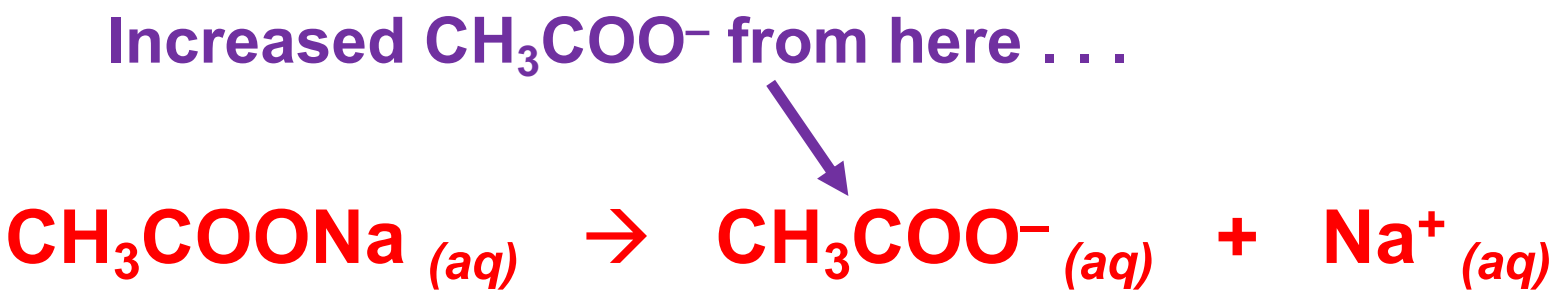
. . . And we added acetate (CH_3COONa)?

Well, because CH_3COONa is a strong electrolyte (an ***ionic compound*** that is highly soluble in water), it dissolves freely in water, like this:

So adding CH_3COONa to our system would increase the amount of CH_3COO^-, which would drive the reaction at the top of this slide to the left by ***Le Châtelier's principle***.

Common Ion Effect





So if you have an ***equilibrium reaction*** and add a ***strong electrolyte*** that produces one of the ions on the right side of the ***equilibrium reaction***, then the ***equilibrium reaction*** will be driven to the left. This is called the ***common-ion effect***.

Common Ion Effect

- 0.50M HCl is added to a solution of $PbCl_2$. What is the new ***molar solubility*** of $PbCl_2$? (***K_{sp}*** = **2.5×10^{-4}**)

Determine if Precipitation Will Occur

For ***precipitation problems***, you don't usually need an ICE table.

Instead, just write the balanced reaction, write the ***solubility expression***, plug in the concentration values, and see if your ***Q*** is larger than K_{sp}.

If $Q > K_{sp}$, you have precipitation. If $Q < K_{sp}$, then you do NOT have precipitation.

Determine if Precipitation Will Occur

- 1×10^{-2} M $Cu(NO_3)_2$ was added to $NaIO_3$ to a final concentration of 6.0×10^{-3}. Does a precipitate form? (K_{sp} of $Cu(IO_3)_2$ $= 3.6 \times 10^{-6}$)