Where have we been and where are we going?

Unit A - Stoichiometry
Unit D - Gases
Unit B - Reactions & Electrochemistry
Unit F - Equilibrium
Unit C - Thermo
Unit E - Kinetics
Unit G - Acid Base Equilibrium
Unit H - Quantum
Unit I - Bonding & Geometry
Unit J - IPFs (InterParticle Forces)

General Equi ⇆ librium

Unit F

Completion of Reactions

- Up until now, you may have been lead to believe that all chemical reactions go to completion, until one reactant or the other runs out.
- While this is true for your favorite reaction type, combustion, it is NOT true for many, many other reactions.
- The state in which a reaction seems to stop before one reactant runs out is called *equilibrium*.

→

What is Equilibrium?

- The state in which the *concentrations* of all the reactants and products *remain constant*.
- However, don't be fooled, although it may appear as if everything has stopped, at the molecular level there is frantic activity. It is a *dynamic equilibrium*.
- This is a state in which the rate of the *forward* reaction *equals* the rate of the *reverse* reaction.

The equilibrium constant, K

$R \longrightarrow$

$R \overset{\leftarrow}{\longrightarrow} P$

$R \leftrightarrows P$

$R \rightleftarrows P$

$R \overset{\longleftarrow}{\scriptstyle\rightarrow} P$

$\longleftarrow P$

- The equilibrium position may not be in the middle (in fact it is usually NOT in the middle).
- Remember that equilibrium occurs when the forward and reverse rates are equal $\rightleftarrows$ not necessarily when there are equal quantities of reactants and products
- The equilibrium constant, K, (a ratio) will tell us the “equilibrium position” or extent of the reaction.

$$K = \frac{[P]}{[R]}$$

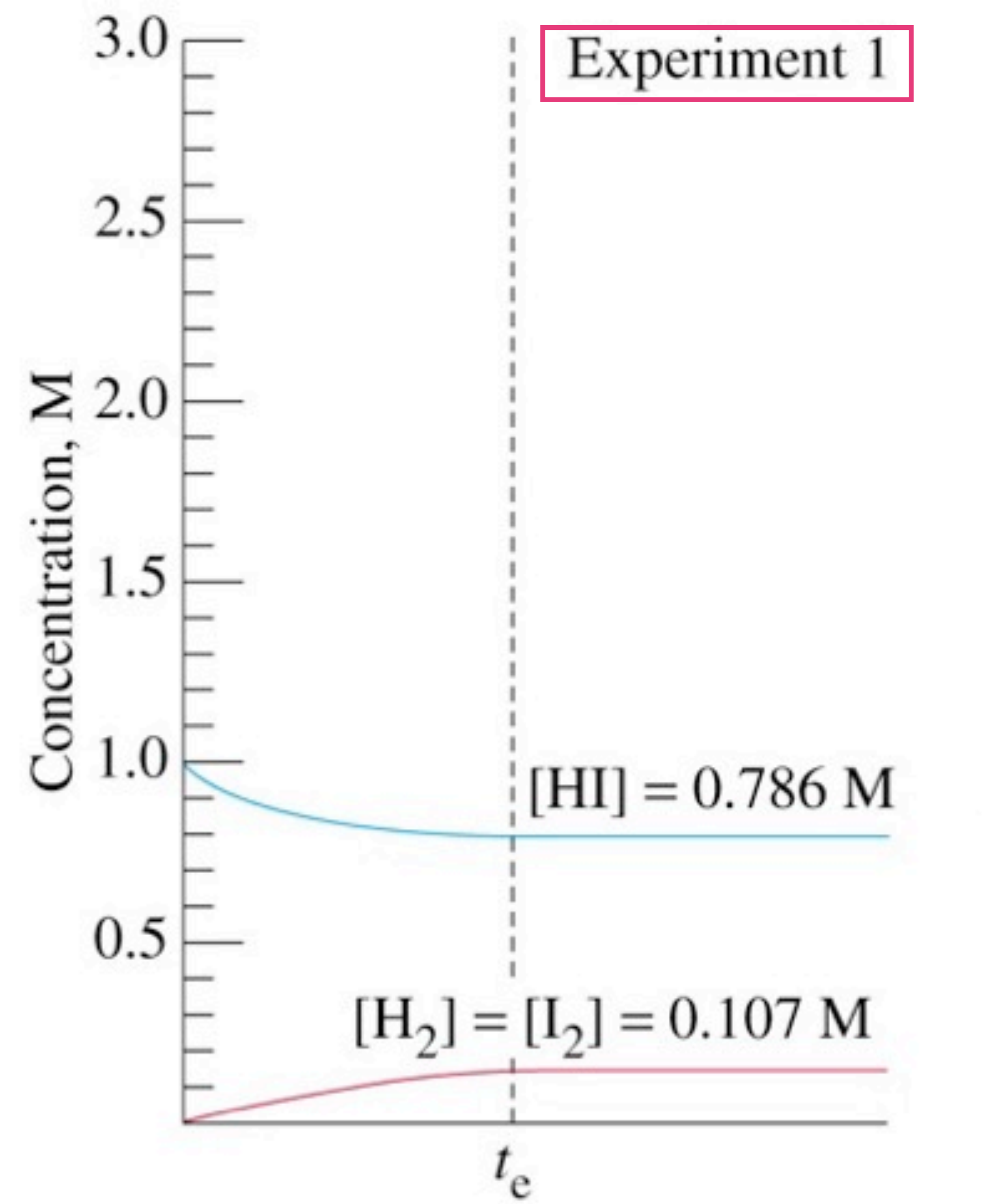
- The equilibrium position can be reached from either direction starting with any quantities. But K (the ratio) will be constant.

$$K = \frac{[P]}{[R]}$$

$2HI_{(g)} \rightleftarrows H_{2(g)} + I_{2(g)}$

Consider the decomposition reaction above in which concentrations were monitored over time.

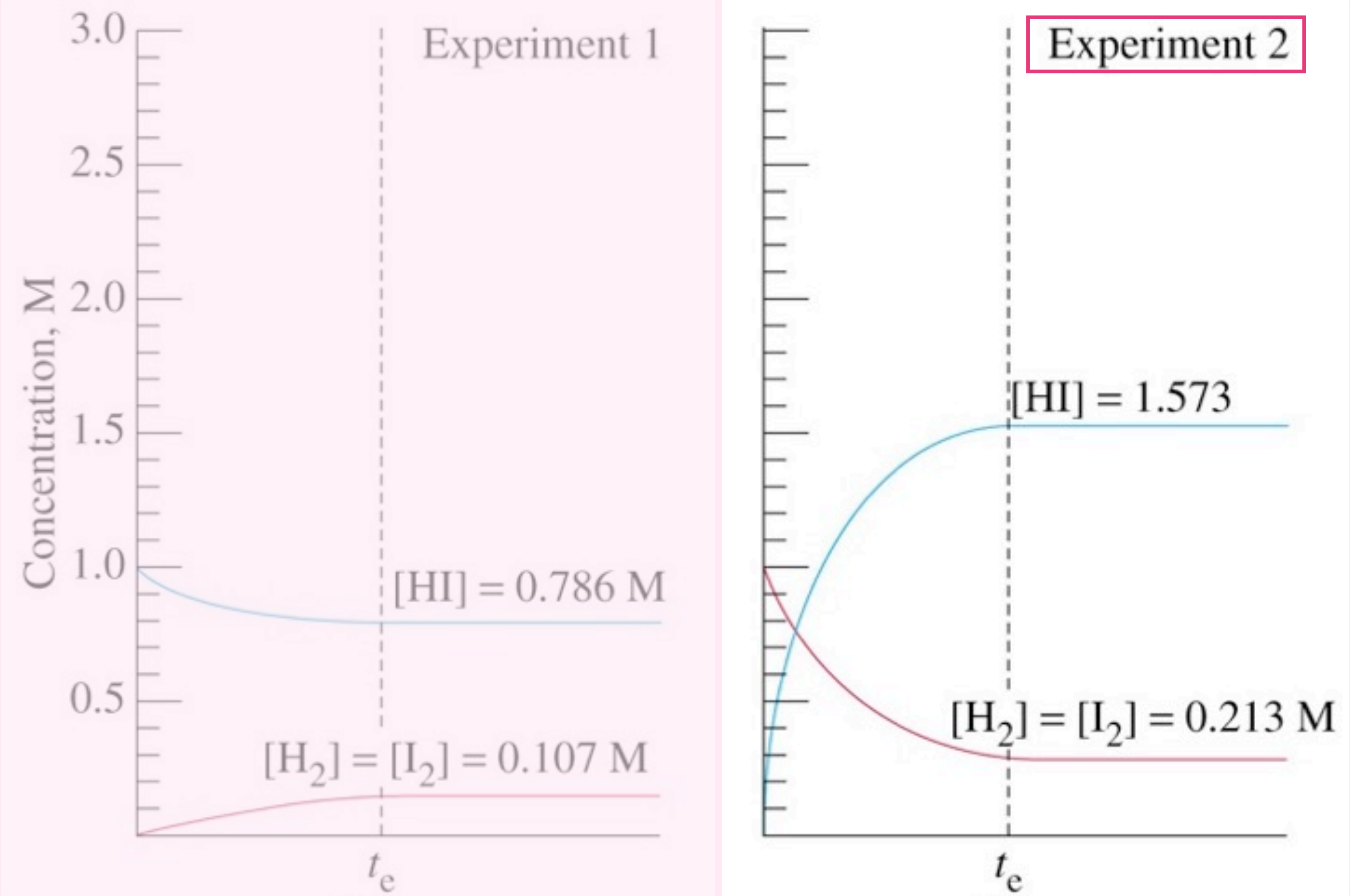
1. Exp 1: 1 M of HI, none of H_2 and I_2



$2HI_{(g)} \rightleftarrows H_{2(g)} + I_{2(g)}$

Consider a second trial with different starting quantities

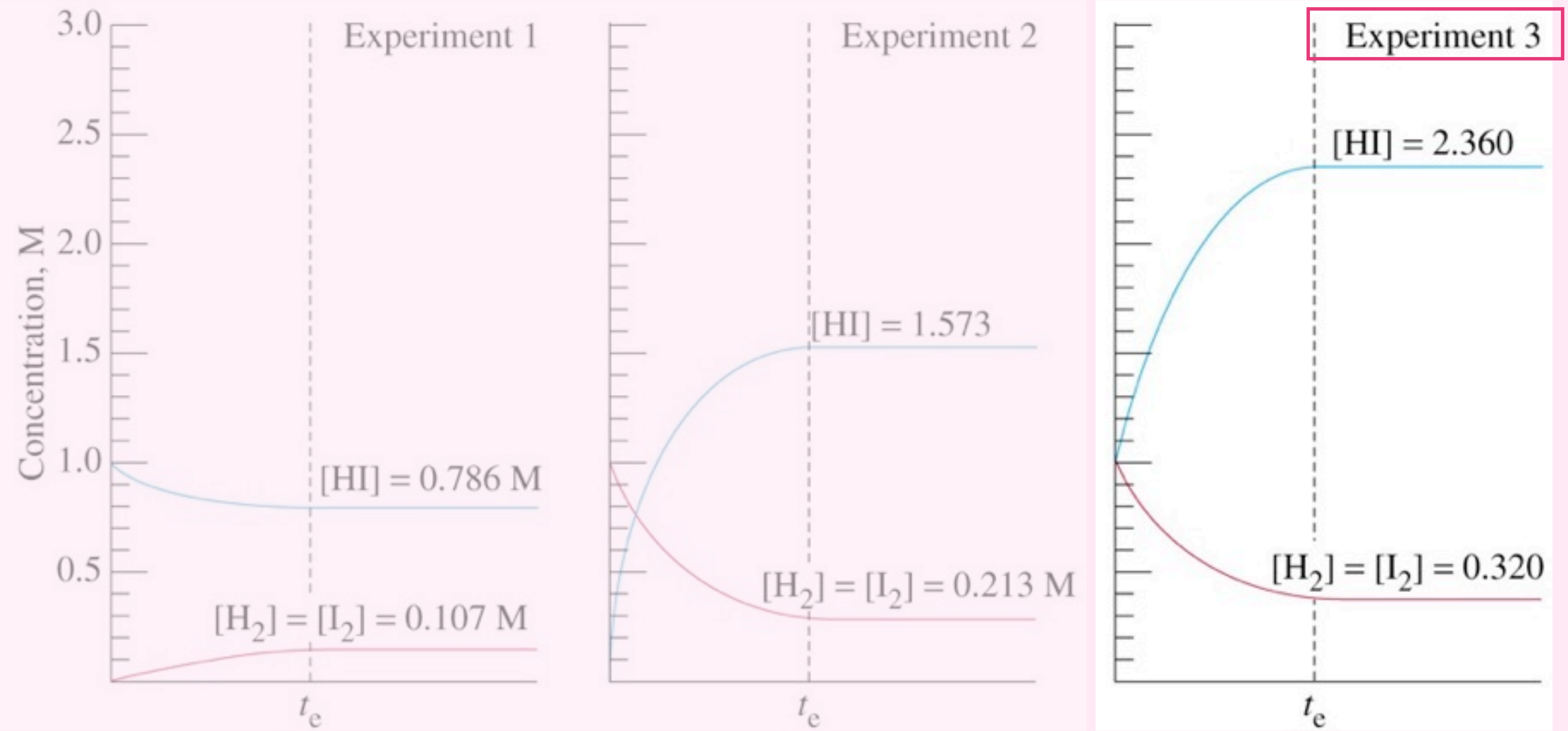
1. Exp 1: 1 M of HI, none of H_2 and I_2
2. Exp 2: 1 M each of H_2 and I_2 , none of HI



$2HI_{(g)} \rightleftarrows H_{2(g)} + I_{2(g)}$

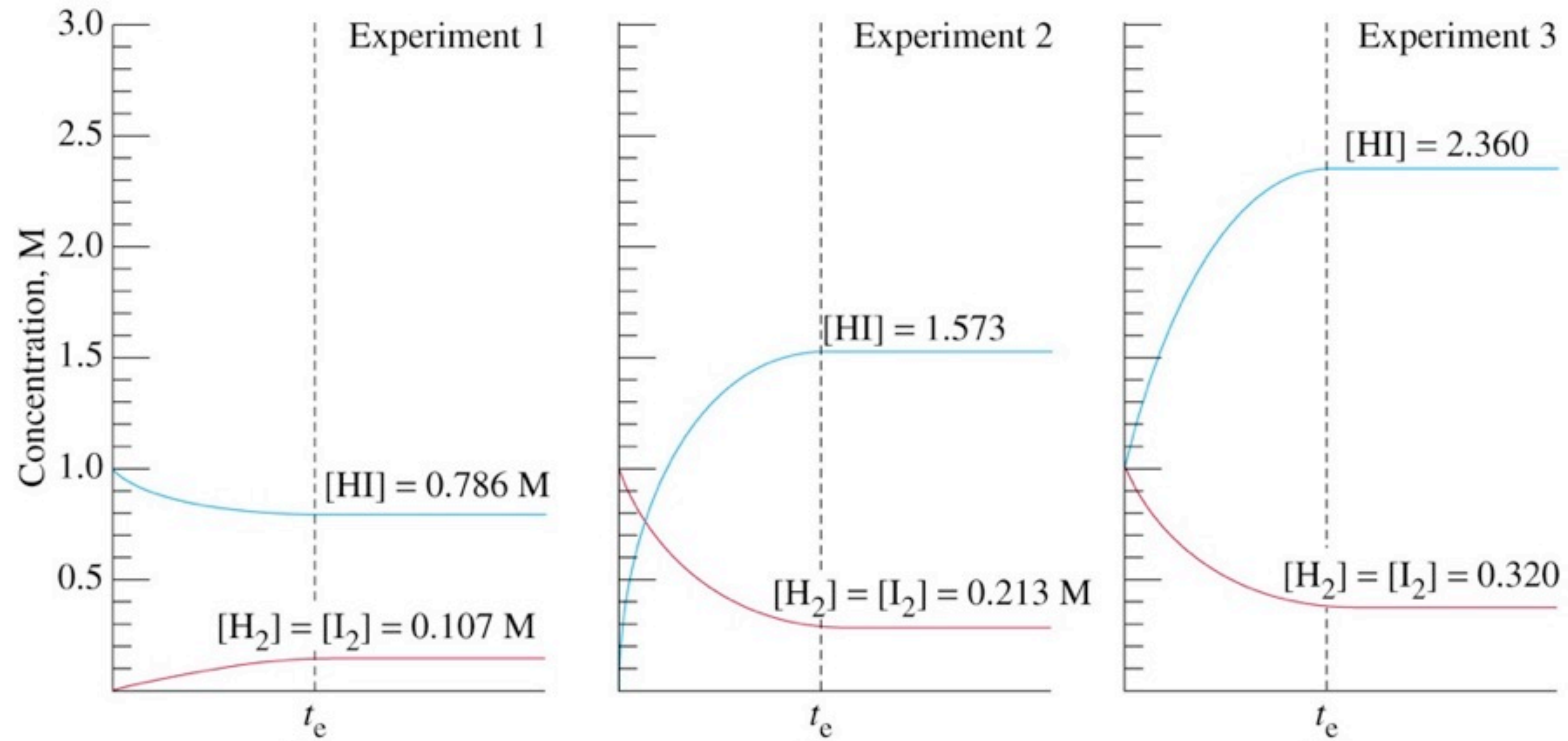
Consider three separate trials with different starting quantities

1. Exp 1: 1 M of HI, none of H_2 and I_2
2. Exp 2: 1 M each of H_2 and I_2 , none of HI
3. Exp 3: 1 M of all three, H_2 , I_2 and HI



After Reaching Equilibrium...

- All three trials will have *different quantities* when the system reaches equilibrium.
- On first inspection, there appears to be no relationship between these equilibrium concentrations, however....



Let’s calculate the Equilibrium Konstant

- Write an Equilibrium Expression

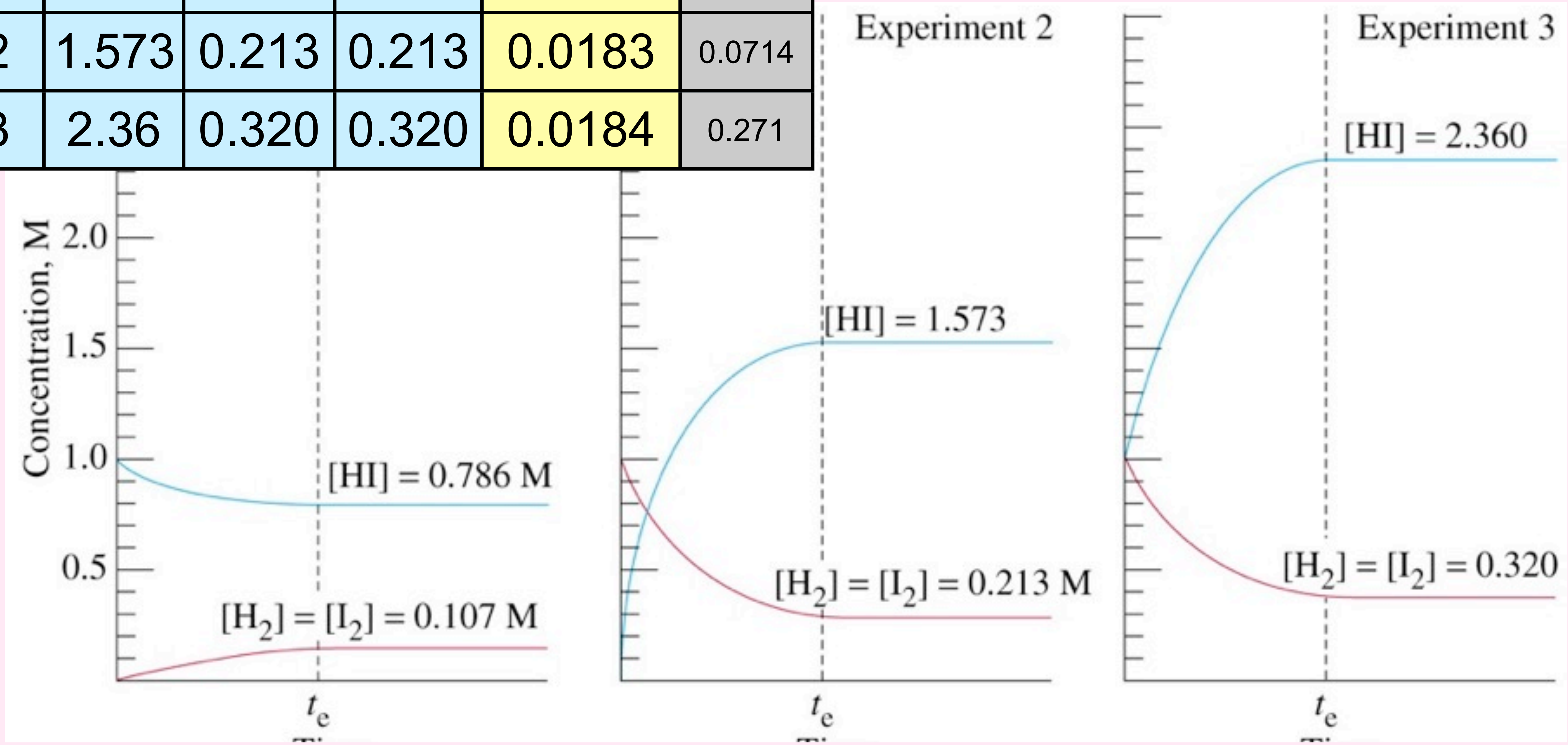
$$K_{eq} = \frac{[H_2]\,[I_2]}{[HI]^2}$$

$$2HI \rightleftarrows H_2 + I_2$$

- Calculate K_{eq} for each Experiment.

Ex	[HI]	$[H_2]$	$[I_2]$	K_{eq}	$notK \frac{[H_2][I_2]}{[HI]}$
1	0.786	0.107	0.107	0.0185	0.0146
2	1.573	0.213	0.213	0.0183	0.0714
3	2.36	0.320	0.320	0.0184	0.271

$$\cancel{K = \frac{[H_2][I_2]}{[HI]}}$$



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Mass Action Expression, Q

- For any reaction:
  - ✓ $aA + bB \leftrightarrows cC + dD$
- A mass action expression can be written:
  - ✓ The *reaction quotient,* Q = $\dfrac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$
- If the reaction is at equilibrium, Q is equal to *K*
  - ✓ *and K (aka K_{eq})* = $\dfrac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$ *the equilibrium expression*
- Unlike rate laws, the equilibrium expression depends only on the stoichiometry *not* on the mechanism.

Practice Writing Equilibrium Expressions

- Let's stop and do problem # 1

1. Write an expression *(yes, I know, it's actually an equation, but AP will request an expression and expect an equation)* for the equilibrium constant for each of the following chemical equations.

a. $SbCl_{5(g)} \leftrightarrows SbCl_{3(g)} + Cl_{2(g)}$

b. $2\ BrNO_{(g)} \leftrightarrows 2\ NO_{(g)} + Br_{2(g)}$

Practice Writing Equilibrium Expressions

- problem # 1

a. $SbCl_{5(g)} \leftrightharpoons SbCl_{3(g)} + Cl_{2(g)}$

$$K_{eq} = \frac{[SbCl_3][Cl_2]}{[SbCl_5]}$$

b. $2\ BrNO_{(g)} \leftrightharpoons 2\ NO_{(g)} + Br_{2(g)}$

$$K_{eq} = \frac{[NO]^2[Br_2]}{[BrNO]^2}$$

What does the Subscript on $K_?$ tell us?

[square brackets] or (parentheses)?

...and what are the units on the *K* value?

What does the magnitude of *K* tell us?

Just how constant is *K*?

K_{eq} vs K_p and K_c

- K or K_{eq} is a generic term that can symbolize any equilibrium constant.
- It's helpful if you distinguish which K_{eq} you are referring to.
  - ✓ K_p if calculated with gases measured in atmospheres (atm)
  - ✓ K_c if calculated for substance measured in molarity [M]
- However, some books (like ours) do *not* always differentiate for K_p and use K_{eq} almost exclusively to mean K_p or K_c. You will know by the context of the problem which K (K_p or K_c) you are calculating.
  - ✓ If the substances are gases, assume when they say K_{eq}, they mean K_p
- Later in this unit we will study K_{sp}
- In the next unit we will learn about K_a, K_b, K_w

→

Square Brackets [ ] or parentheses ( ) ?

- *AP can be a bit particular on this one.*
- If you are asked to write the equilibrium expression for K_c you must use square brackets

$$K_c = \frac{[SbCl_3][Br_2]}{[SbCl_5]}$$

- If you are asked to write the equilibrium expression for K_p you must use parentheses.

$$K_p = \frac{\left(P_{SbCl_3}\right)\left(P_{Br_2}\right)}{\left(P_{SbCl_5}\right)}$$

Practice Writing Equilibrium Expressions

- problem # 1

a. $SbCl_{5(g)} \leftrightharpoons SbCl_{3(g)} + Cl_{2(g)}$

$$K_c = \frac{[SbCl_3][Cl_2]}{[SbCl_5]} \qquad K_p = \frac{\left(P_{SbCl_3}\right)\left(P_{Cl_2}\right)}{\left(P_{SbCl_5}\right)}$$

b. $2\ BrNO_{(g)} \leftrightharpoons 2\ NO_{(g)} + Br_{2(g)}$

$$K_c = \frac{[NO]^2[Br_2]}{[BrNO]^2} \qquad K_p = \frac{\left(P_{NO}\right)^2\left(P_{Br_2}\right)}{\left(P_{BrNO}\right)^2}$$

Units on K_{eq} ?

- None

- They would vary from constant to constant.

$$\frac{[NO]^2[Br_2]}{[BrNO]^2} \Rightarrow M \qquad \frac{[D]^2}{[A]^2[C]} \Rightarrow M^{-1} \qquad \frac{[A]^2}{[B]^4[C]} \Rightarrow M^{-3} \qquad [X]^2 \Rightarrow M^2$$

- They wouldn’t have any meaning or purpose, so we leave them off.

  There is a formal reason that allows us to leave them off, we don’t really care.

- *One of the few naked numbers!*

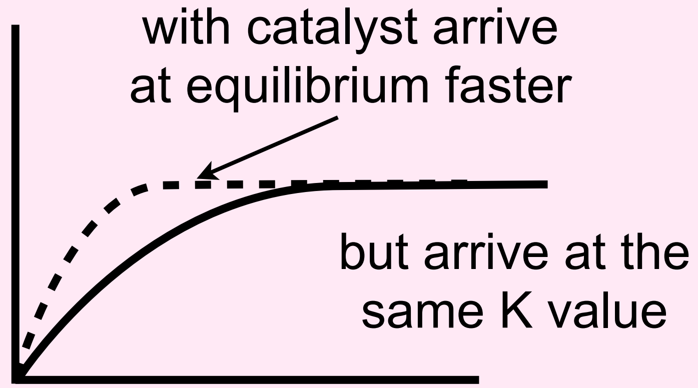
  (Along with Absorbance and pH)

The Equilibrium *K*onstant

- The magnitude of *K* is an indication of how far a reaction proceeds toward product at a given temperature.
- Some reactions so favor the products that the reaction appears to have “gone to completion” − Equilibrium lies *far to the right*.
  - ✓ *K* will be large, perhaps 1 x 10^{25}
- A system that appears that there is “no reaction” may actually be at equilibrium *far to the left*.
  - ✓ *K* will be small, perhaps as small as 5 x 10^{-30}
- When significant quantities of both reactant and product are present, *K* will have an intermediate value.

Just How *Constant* is the Equilibrium K*onstant?*

- The constant is unique to each reaction.
- The constant does *vary* with temperature.
- It does *not* depend on the initial amounts of reactants or products.
- It is *not* affected by the presence of any other materials, *not even a catalyst*.



- Equilibrium can be reached from either the forward or reverse directions.

Distinguish Equilibrium *Konstant* from Equilibrium *Position*

- For a particular temperature, there is only *one equilibrium constant*.
- But there are an *infinite* number of sets of various equilibrium concentrations, resulting in *many equilibrium positions*.

The Relationship Between the Equilibrium Constant and the Balanced Chemical Equation

Stoichiometry of Reactions
Reversing Reactions
Hess’ Law - Adding Reactions

K_{eq} and Direction of Reaction

- For the forward Rx: 2 A + B ⇆ 3 C
  - ✓ $K_{eq\ fwd} = \frac{[C]^3}{[A]^2[B]}$
- For the reverse Rx: 3 C ⇆ 2 A + B
  - ✓ $K_{eq\ rvs} = \frac{[A]^2[B]}{[C]^3}$
- Thus $K_{eq\ rvs} = \frac{1}{K_{eq\ \mathrm{fwd}}}$
- When a reaction is reversed, take the inverse of the K_{eq} value.

K_{eq} and Stoichiometry

- For the Rx: $2\text{ A} + \text{B} \leftrightarrows 3\text{ C}$

  ✓ $K_{eq} = \dfrac{[C]^3}{[A]^2[B]}$

- For Rx doubled: $4\text{ A} + 2\text{ B} \leftrightarrows 6\text{ C}$

  ✓ $K_{eq\ doubled} = \dfrac{[C]^6}{[A]^4[B]^2}$ which $= \left(\dfrac{[C]^3}{[A]^2[B]}\right)^2$

- Thus $K_{eq\ doubled} = (K_{eq})^2$

- When the coefficients are changed by some factor, *n*, the K_{eq} is raised to that same n^{th} factor.

- Don't forget your exponent rules $x^{1/2} = \sqrt{x}$

Hess' Law of Adding Reactions

- Chemists have learned that reactions can "add" together to produce other reactions.
- $2\,S + \overset{2}{\cancel{3}}\,O_2 \rightarrow \cancel{2\,SO_3}$
- $\cancel{2\,SO_3} \rightarrow 2\,SO_2 + \cancel{O_2}$
- These two reactions add to produce a third reaction.
- $2\,S + 2\,O_2 \rightarrow 2\,SO_2$
- which of course can be reduced to: $S + O_2 \rightarrow SO_2$
- This is called Hess' Law

K_{eq} and Hess' Law

- Suppose you knew *K* for these two reactions:
  - ✓ Rx$_1$: 4B + C $\leftrightarrows$ 2A K_{eq1} = 0.5 $K_{eq1}=\frac{[A]^2}{[B]^4[C]}=0.5$
  - ✓ Rx$_2$: 2B + C $\leftrightarrows$ D K_{eq2} = 3 $K_{eq2}=\frac{[D]}{[B]^2[C]}=3$

Write the equilibrium expressions for Rx$_1$ and Rx$_2$

- and suppose you wanted to know K for this reaction
  - ✓ Rx$_{net}$: 2A + C $\leftrightarrows$ 2D $K_{net}=\frac{[D]^2}{[A]^2[C]}$

Write the equilibrium expression for this Rx$_{net}$

- Let's manipulate Rx$_1$ & Rx$_2$ to produce the Rx$_{net}$ above
  - ✓ Rx$_1$ reverse : 2A $\leftrightarrows$ 4B + C $K_{eq1rev}=\frac{[B]^4[C]}{[A]^2}$ $K_{eq\ rvs}=\frac{1}{K_{eq1}}=2$
  - ✓ Rx$_2$x2 : 4B + 2C $\leftrightarrows$ 2D $K_{eq2\times2}=\frac{[D]^2}{[B]^4[C]^2}=\left(\frac{[D]}{[B]^2[C]}\right)^2$ $K_{eq\ Rx\ x2}=(K_{eq2})^2=9$
- Add Rx$_1$ and Rx$_2$ = Rx$_{net}$

$$\frac{[B]^4[C]}{[A]^2}+\frac{[D]^2}{[B]^4[C]^2}\neq\frac{[D]^2}{[A]^2[C]}$$

but.....

$$\frac{[B]^4[C]}{[A]^2}\times\frac{[D]^2}{[B]^4[C]^2}=K_{net}=\frac{[D]^2}{[A]^2[C]}$$

  - ✓ Thus $K_{eq\ net}$ = ($K_{eq\ rvs}$, 2)($K_{eq\ x2}$, 9) = 18

- When using Hess' Law, the reactions are added, but the K_{eq} values are multiplied.

The relationship between K and the equilibrium equation it represents

- Let's stop and do problem # 2

2. $2\,SO_{2(g)} + O_{2(g)} \leftrightharpoons 2\,SO_{3(g)}$ $K = 261$ at 727ºC

Using the information above, calculate the equilibrium constant for the following reactions at 727ºC.

a. $2\,SO_{3(g)} \leftrightharpoons 2\,SO_{2(g)} + O_{2(g)}$

This is the reverse of the reaction, thus

$$K_{reverse} = \frac{1}{261} = 0.00383$$

b. $SO_{2(g)} + \tfrac{1}{2}\,O_{2(g)} \leftrightharpoons SO_{3(g)}$

This is ½× the reaction, thus

$$K_{1/2} = (261)^{1/2} = \sqrt{261} = 16.2$$

The relationship between K and the equilibrium equation it represents

3. Consider the reactions and their respective equilibrium constants:

   $NO_{(g)} + \frac{1}{2} Br_{2(g)} \leftrightharpoons NOBr_{(g)} \quad K_p = 4$

   $2\ NO_{(g)} \leftrightharpoons N_{2(g)} + O_{2(g)} \quad K_p = 2 \times 10^{30}$

   Use the reactions above and their equilibrium constants to predict the equilibrium constant, K_p for the following reaction:

- $N_{2(g)} + O_{2(g)} + Br_{2(g)} \leftrightharpoons 2\ NOBr_{(g)}$

Work it without a calculator.

Rx 1 ×2 $2NO_{(g)} + Br_{2(g)} \leftrightharpoons 2NOBr_{(g)} \quad (K_p)^2 = (4)^2$

Rx 2 rev $N_{2(g)} + O_{2(g)} \leftrightharpoons 2\ NO_{(g)} \quad \frac{1}{K_p} = \frac{1}{2 \times 10^{30}}$

———————————————————————

$N_{2(g)} + O_{2(g)} + Br_{2(g)} \leftrightharpoons 2\ NOBr_{(g)} \quad K_{overall} = \frac{(4)^2}{2 \times 10^{30}} = 8 \times 10^{-30}$

Equilibrium Expression

Which substances are in the Equilibrium Expression?

not (L) or (s)
only (g) and (aq)

Why?

Calculate the concentration of 1000 ml of water.

Calculate the concentration of 1000 ml of water.

- 1000 ml = 1000g

$$Molarity = \frac{moles}{liters}$$

$$1000g \times \frac{1mol}{18g} = 55.6mol$$

$$Molarity = \frac{55.6moles}{1liters} = 55.6M$$

→

Calculate the concentration of 18 ml of water.

Calculate the concentration of 18 ml of water.

$$Molarity = \frac{moles}{liters}$$

- 18 ml = 18g

$$18g \times \frac{1mol}{18g} = 1mol \qquad Molarity = \frac{1moles}{0.018liters} = 55.6M$$

- The concentration of any pure liquid or pure solid is always constant.
- Pure solids and pure liquids, (s) and (L), do not end up in the equilibrium expression.
- Adding more or less of them does NOT change the equilibrium position.

For Reaction $A_{(s)} + B_{(g)} \rightarrow C_{(g)}$

- Write the equilibrium expression for the reaction above.

$$\cancel{K = \frac{[C]}{[A][B]}} \qquad K_c = \frac{[C]}{[B]} \;✓\; \frac{(C)}{(B)} = K_p$$

- What would be the effect on the quantity of C present at equilibrium if a small amount of A (assume negligible effect on volume) were increased?

- NO EFFECT. Equilibrium expressions do *not* include pure liquids or solids, since solid and liquid concentrations are always constant.

Heterogeneous Reactions

and not so heterogeneous equilibria

- Let’s stop and do problem # 4

4. Write an equilibrium expression for each of the following chemical reactions. (Assume gases are measured in atm.)
   a. $CO_3^{2-}{}_{(aq)} + H_2O_{(L)} \leftrightarrows HCO_3^{-}{}_{(aq)} + OH^{-}{}_{(aq)}$

$$K_c = \frac{\left[OH^-\right]\left[HCO_3^-\right]}{\left[CO_3^{2-}\right]}$$

   b. $2\ KClO_{3(s)} \leftrightarrows 2\ KCl_{(s)} + 3\ O_{2(g)}$ $\quad K_p = \left(P_{O_2}\right)^3$

Heterogeneous Reactions

and a truly heterogeneous equilibria,

I’ll bet you will NOT see this on the AP exam.

- continue with problem # 4

4. Write an equilibrium expression for each of the following chemical reaction. (Assume gases are measured in atm.)

   c. $Zn_{(s)} + 2\,H^{+}_{(aq)} \leftrightharpoons Zn^{2+}_{(aq)} + H_{2(g)}$

$$K_{eq} = \frac{\left[Zn^{2+}\right]\left(P_{H_2}\right)}{\left[H^{+}\right]^{2}}$$

K_{eq} and Condensed Phases

- Reactions that involve more than one phase are called *heterogeneous* equilibrium.

- But remember that if a *pure solid* or a *pure liquid* is in an equilibrium reaction, they *do not show up* in the equilibrium expression.

- So a heterogeneous equilibrium expression would only include gases and aqueous solutions end up in the same equation, and odds are you will not likely see this on the AP exam.

- Not that these reactions are unusual, it's just that we don't generally study them in an equilibrium context.
  $2Al_{(s)} + 6H^+_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3\,H_{2(g)}$

→

Calculating Equilibrium Constants

Calculate K_p for the following reaction *given the equilibrium quantities*:

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

No calculator

$SO_2 = 2$ atm, $O_2 = 3$ atm, $SO_3 = 12$ atm

Calculate K for the following reaction given the equilibrium quantities

$2SO_{2(g)} + O_{2(g)} \rightleftarrows 2SO_{3(g)}$ No calculator

$SO_2 = 2$ atm, $O_2 = 3$ atm, $SO_3 = 12$ atm

$$K_p = \frac{(P_{SO_3})^2}{(P_{SO_2})^2(P_{O_2})} \qquad K_p = \frac{(12)^2}{(2)^2(3)} = 12$$

→

What if you are asked to calculate *K*, but you are NOT given the equilibrium concentrations?

NH_3 is placed in a flask with a partial pressure of 3 atm, and is allowed to decompose into its elemental gases. At equilibrium, the partial pressure of nitrogen is 0.25 atm. *Calculate the K_p at this temp for the equation below.*

$$2\ NH_{3(g)} \quad \leftrightarrows \quad N_{2(g)} \quad + \quad 3\ H_{2(g)}$$

- *Write the Equilibrium Expression.*

What if you are asked to calculate *K*, but you are NOT given the equilibrium concentrations?

NH_3 is placed in a flask with a partial pressure of 3 atm, and is allowed to decompose into its elemental gases. At equilibrium, the partial pressure of nitrogen is 0.25 atm. *Calculate the K_p at this temp for the equation below.*

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

$$K_p = \frac{(P_{H_2})^3(P_{N_2})}{(P_{NH_3})^2}$$

We need to organize the the information, and calculate the equilibrium concentrations.

→

NH_3 is placed in an empty flask with a partial pressure of 3 atm, and is allowed to decompose into its elemental gases. At equilibrium, the partial pressure of nitrogen is 0.25 atm. Calculate the K_p at this temp.

- $2\ NH_{3(g)} \leftrightarrows N_{2(g)} + 3\ H_{2(g)}$ $$K_p = \frac{(P_{H_2})^3 (P_{N_2})}{(P_{NH_3})^2}$$
- Use the Grid below to organize the information

R	$2\ NH_{3(g)}$ $\leftrightarrows$	$N_{2(g)}$ +	$3\ H_{2(g)}$
I			
C			
E			

NH_3 is placed in an empty flask with a partial pressure of 3 atm, and is allowed to decompose into its elemental gases. At equilibrium, the partial pressure of nitrogen is 0.25 atm. Calculate the K_p at this temp.

» $2\ NH_{3(g)} \leftrightarrows N_{2(g)} + 3\ H_{2(g)}$

$$K_p = \frac{(P_{H_2})^3(P_{N_2})}{(P_{NH_3})^2}$$

» Use the Grid below to organize the information

R	$2\ NH_{3(g)}$ $\leftrightarrows$	$N_{2(g)}$ +	$3\ H_{2(g)}$
I	3 atm	0 atm	0 atm
C	-0.5 atm	+0.25 atm	+0.75 atm
E	2.5 atm	0.25 atm	0.75 atm

$$K_p = \frac{(0.75)^3(0.25)}{(2.5)^2} = 0.017$$

Percent *remaining*, Percent *reacted*

Don't get tripped up by the language!

- The concentration of some molecule is 0.50 M initially and after equilibrium is reached, 30% of the molecule *remains* in the flask. What is the concentration of this molecule at equilibrium?

$$\% = \frac{part}{total}$$

$$0.50M \times 0.30 = 0.15M$$

- There is 0.080 mol of some molecule B in a 200 ml flask initially, 40% of the molecule has *reacted*. What is the concentration of this molecule at equilibrium?

$$\frac{0.080mol \times 0.60}{0.2L} = 0.24M$$

4 moles of gaseous NO_2 are placed in a 1.0 L container and maintained at a constant temperature. After equilibrium was established, it was found that 25% of the NO_2 remains after dissociating into NO and O_2 gases. Calculate the equilibrium constant, K_c.

...or the same problem could read like this....

→

4 moles of gaseous NO_2 are placed in a 1.0 L container and maintained at a constant temperature. After equilibrium was established, it was found that 25% of the NO_2 remains after dissociating into NO and O_2 gases. Calculate the equilibrium constant, K_c.

4 moles of gaseous NO_2 are placed in a 1.0 L container and maintained at a constant temperature. After equilibrium was established, it was found that 75% of the NO_2 had dissociated into NO and O_2 gases. Calculate the equilibrium constant, K_c.

Write a balanced equation, then write an equilibrium expression, then set up a grid (a RICE Box) to organize the information.

$2NO_2 \rightarrow 2NO + O_2$

$$K_c = \frac{[NO]^2[O_2]}{[NO_2]^2}$$

→

4 moles of NO_2 are placed in a 1.0 L container and maintained at a constant temperature. After equilibrium was established, it was found that 75% of the NO_2 had dissociated into NO and O_2. Calculate the equilibrium constant, K_c.

What does 75% dissociation tell us?

R	$2NO_2 \rightarrow$	$2NO$	O_2
I	4	0	0
C	-3		
E			

$$K_c = \frac{[NO]^2[O_2]}{[NO_2]^2}$$

4 moles of NO_2 are placed in a 1.0 L container and maintained at a constant temperature. After equilibrium was established, it was found that 75% of the NO_2 had dissociated into NO and O_2. Calculate the equilibrium constant, K_c.

Now what can we deduce?

R	$2NO_2 \rightarrow$	$2NO$	O_2
I	4	0	0
C	-3	+3	+1.5
E	1	3	1.5

$$K_c = \frac{[NO]^2[O_2]}{[NO_2]^2}$$

→

4 moles of NO_2 are placed in a 1.0 L container and maintained at a constant temperature. After equilibrium was established, it was found that 75% of the NO_2 had dissociated into NO and O_2. Calculate the equilibrium constant, K_c.

Now fill in the equilibrium expression

R	$2NO_2 \rightarrow$	2NO	O_2
I	4	0	0
C	-3	+3	+1.5
E	1	3	1.5

$$K_{eq} = \frac{[3]^2[1.5]}{[1]^2} = 13.5$$

→

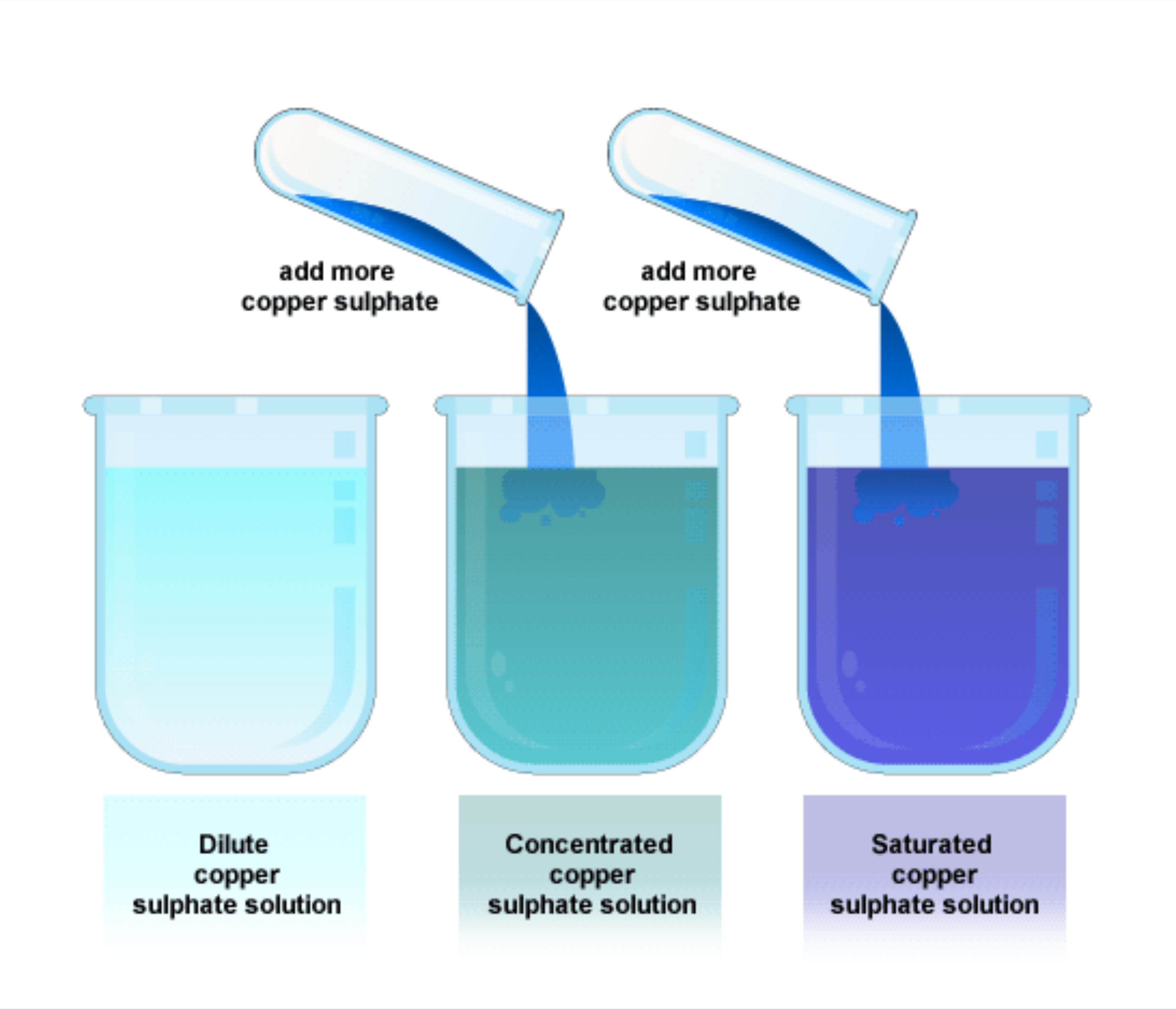
Lab Review

Color and Concentration

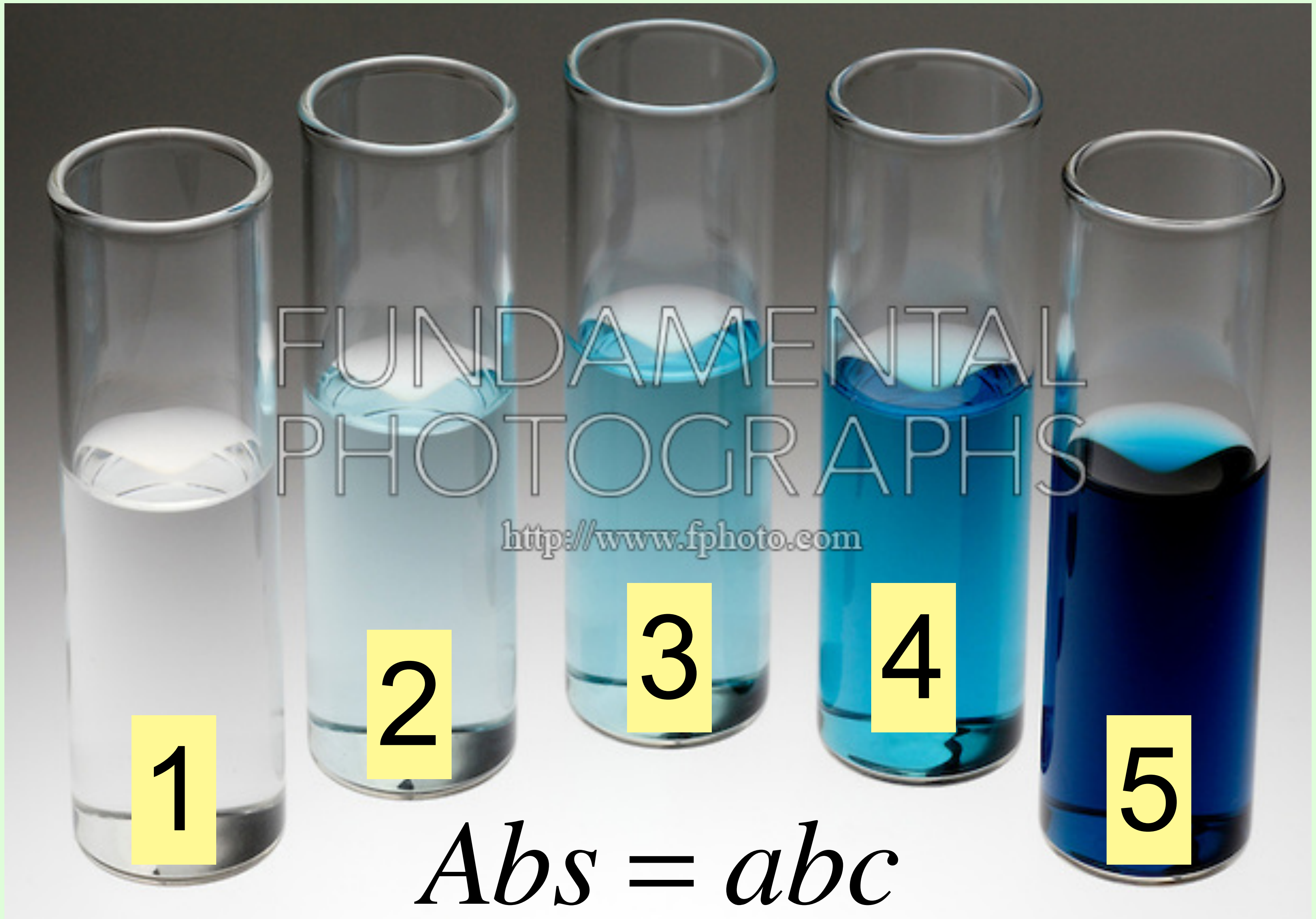
$$Fe^{3+} + SCN^{-} \rightarrow FeSCN^{2+}$$

Which copper(II) sulfate solution is most concentrated?

Concentration

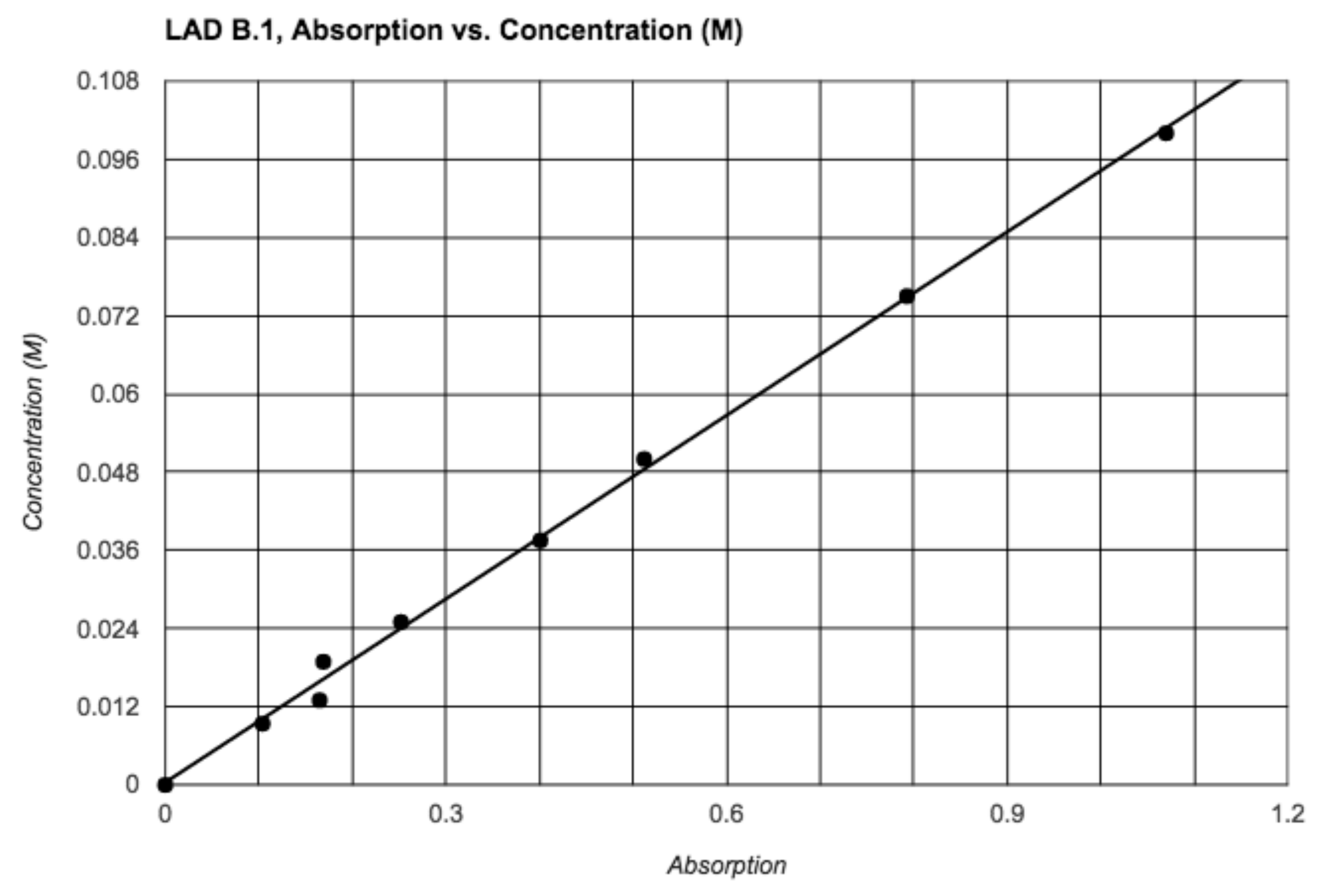


Which solution would have the highest absorbance, (A) using a visible spectrophotometer?



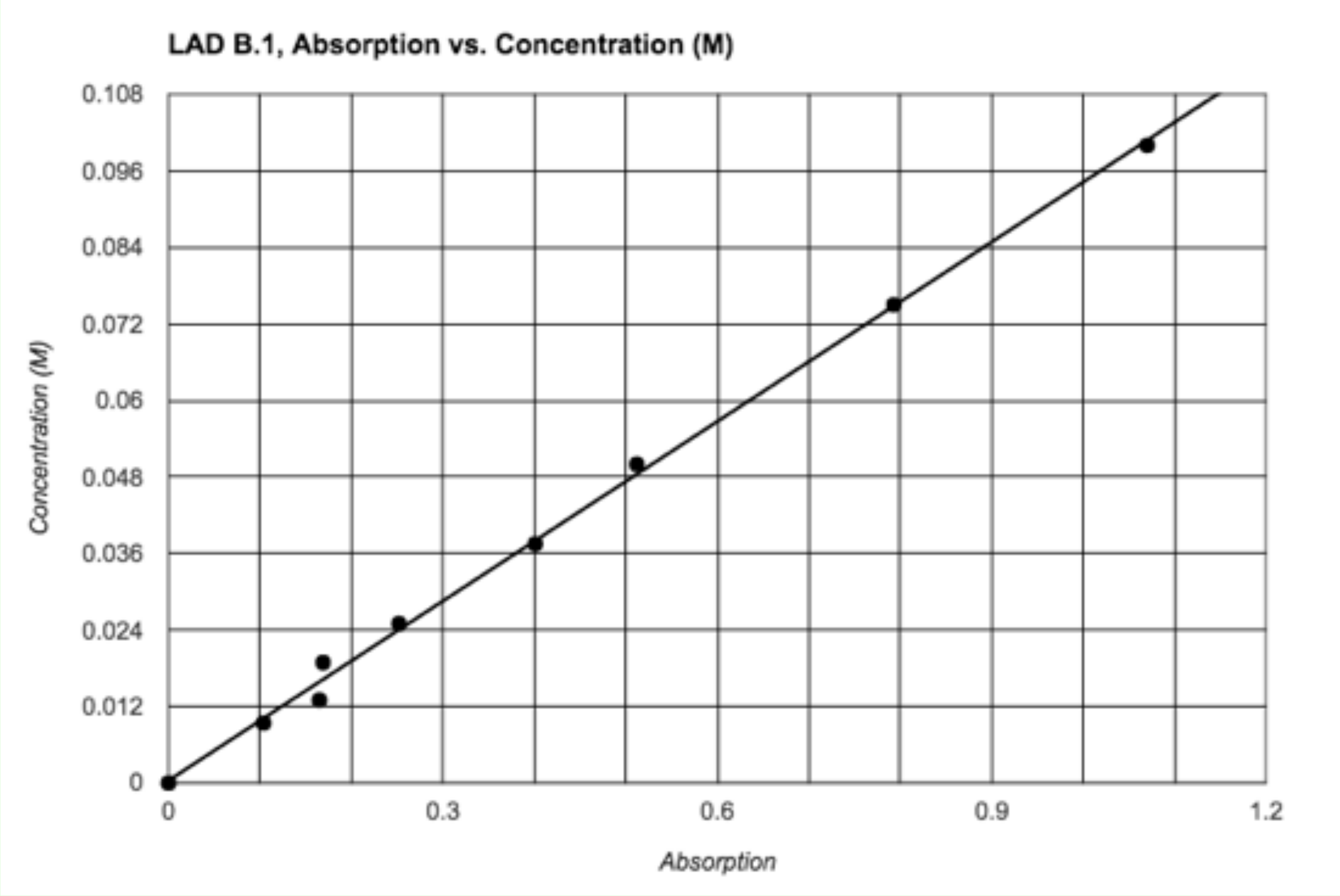
$$Abs = abc$$

What does this graph tell us about the relationship between absorbance and concentration?



What does this graph tell us about the relationship between absorbance and concentration?

- A solution of 0.750 M has an absorbance of 0.793
- Calculate the concentration of the solution that has an absorbance of 0.550



Lab F1
Calculating the Equilibrium Constant

$$\mathrm{Fe^{3+}} + \mathrm{SCN^{-}} \rightarrow \mathrm{FeSCN^{2+}}$$

Iron(III) nitrate nonahydrate reacted with potassium thiocyanate

- $Fe(NO_3)_3 \cdot 9H_2O$ + KSCN
- produces $FeSCN^{2+}$
- The NET ionic equation is:

$$Fe^{3+} + SCN^{-} \rightarrow FeSCN^{2+}$$

- Write the Equilibrium Expression

We can use color to help us determine the concentration of a solution

$$Fe^{3+} + SCN^{-} \rightarrow FeSCN^{2+}$$

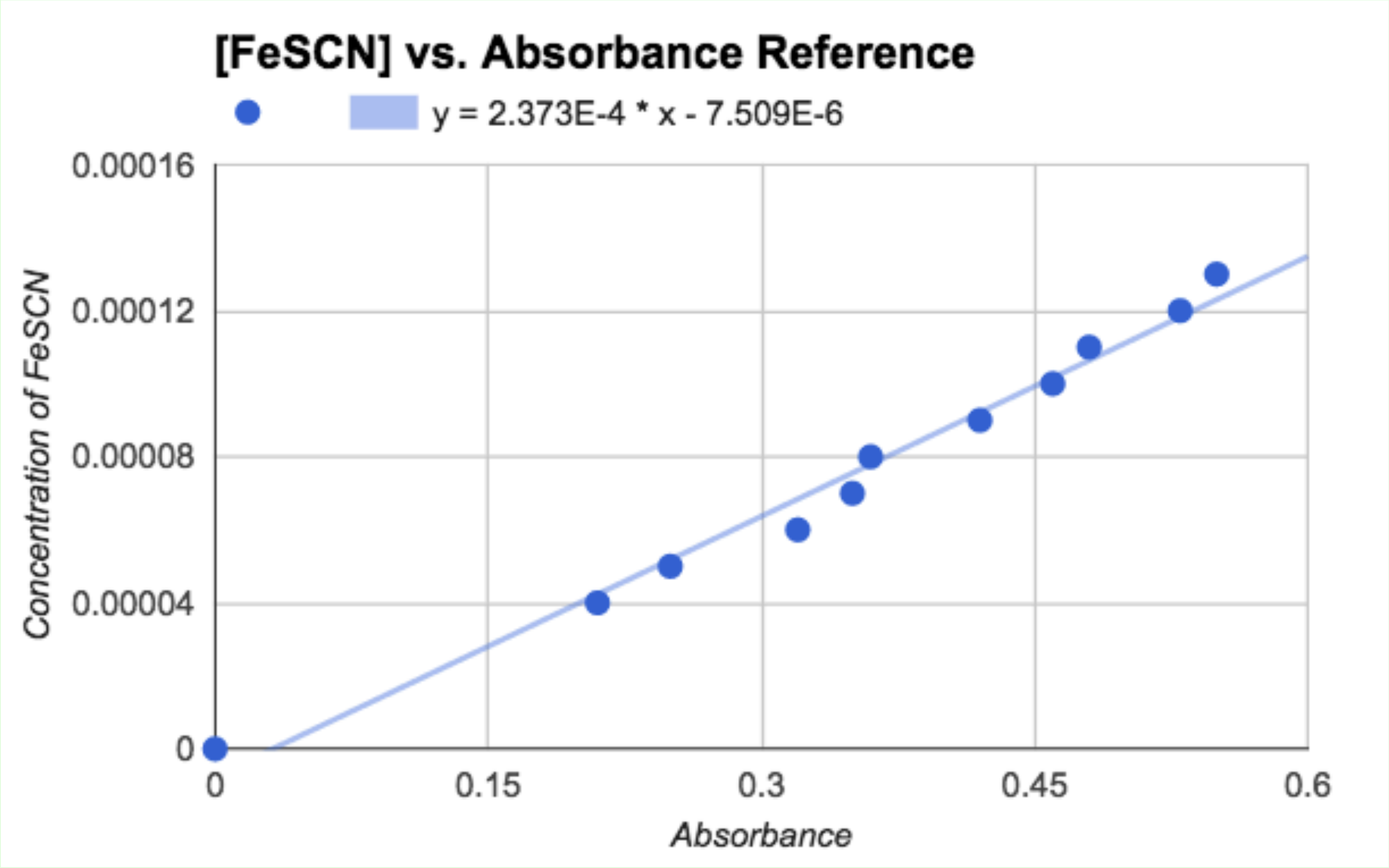
pale purple

colorless

red

- What can you tell me about the concentration of the following solutions containing the same red-colored compound?

Absorbance of color and concentration are linearly related



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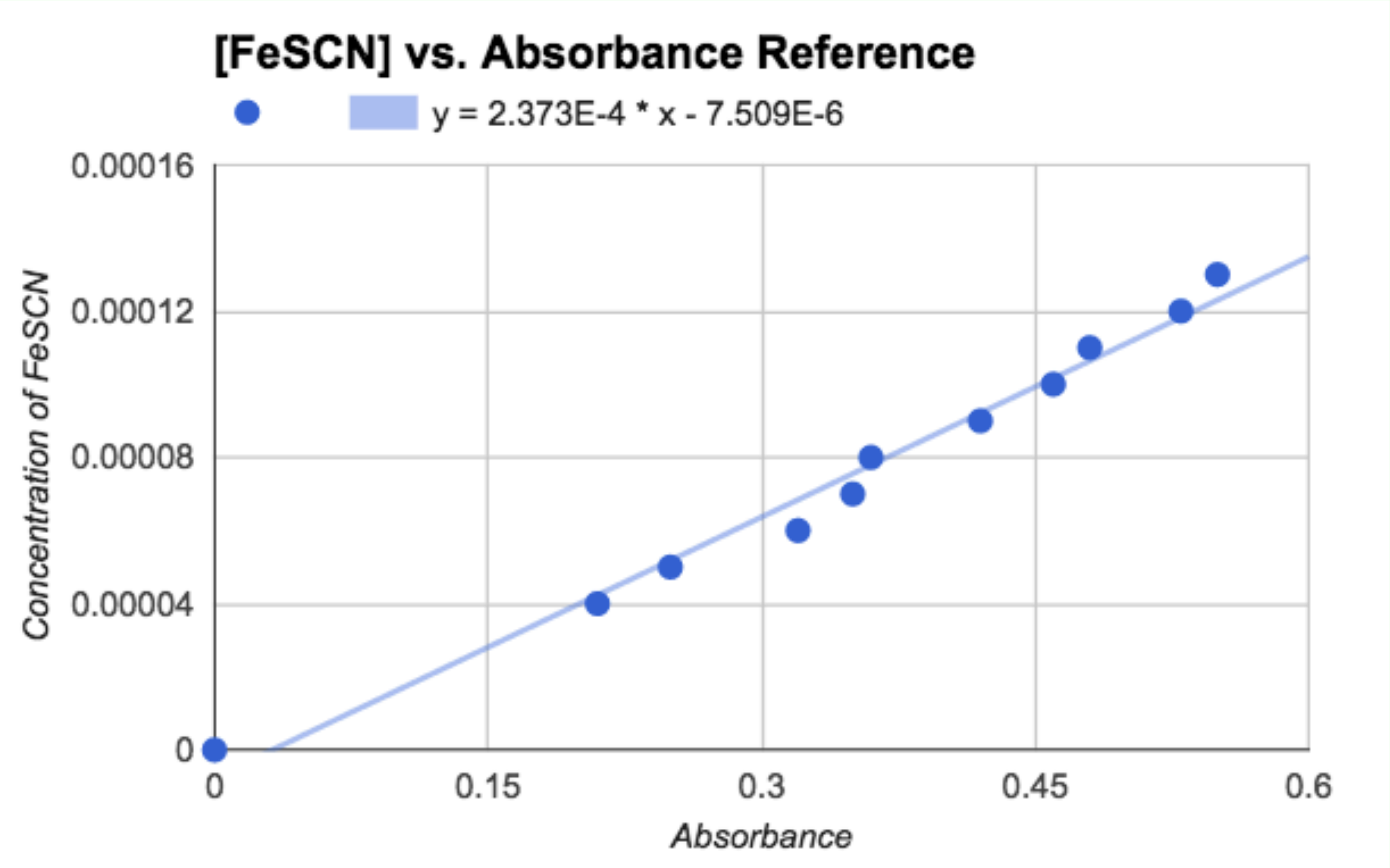

Absorbance of color and concentration are linearly related

- Let’s measure the absorbance of our known standard:

Absorbance = ?

? M

$$MV = MV$$

$$M_cV_c = M_dV_d$$

Any time we pour together two solutions, there is a dilution.

	stock sol'n 0.00200 M	stock sol'n 0.00200 M	
R	Fe^{3+}	SCN^{-} →	$FeSCN^{2+}$
I			0
C			
E			measure

- Calculate the initial, poured together concentration, before any reaction occurs.

$$MV = MV$$

$$M_cV_c = M_dV_d$$

Any time we pour together two solutions, there is a dilution.

R	Fe^{3+} 0.00200 M 5.0 ml	SCN^- 0.00200 M 5.0 ml →	$FeSCN^{2+}$ 0.0 M
I	0.001	0.001	0
C			
E			

- Calculate the initial, poured together concentration, before any reaction occurs.

$$MV = MV$$

$$M_cV_c = M_dV_d$$

Any time we pour together two solutions, there is a dilution.

R	Fe^{3+} 0.00200 M 4.0 ml	SCN^{-} 0.00200 M 6.0 ml →	$FeSCN^{2+}$ 0.0 M
I	0.0008 M	0.0012	0
C			
E			measure

- Calculate the initial, poured together concentration, before any reaction occurs.

React and measure the absorbance

For 0.00016 M the
Absorbance = 0.512

R	Fe^{3+} 0.00200 M 4.0 ml	SCN^{-} 0.00200 M 6.0 ml →	$FeSCN^{2+}$ 0.0 M
I	0.0008 M	0.0012	0
C			
E			measure

- Calculate the equilibrium concentration of the solution just measured.

Make stoichiometric calculations

R	Fe^{3+} 0.00200 M 4.0 ml	SCN^{-} 0.00200 M 6.0 ml	→ $FeSCN^{2+}$ 0.0 M
I	0.0008 M	0.0012	0
C			
E			measure

- Calculate the change row for all three substances.

Equilibrium Concentrations

R	Fe^{3+} 0.00200 M ? ml	SCN^- 0.00200 M ? ml →	$FeSCN^{2+}$ 0.0 M
I			0
C			
E			measured

- Compute the equilibrium concentrations
- Voila, calculate the equilibrium constant.

$$K_c = \frac{\left[FeSCN^{2+}\right]}{\left[Fe^{3+}\right]\left[SCN^{-}\right]}$$

Standard
Absorbance = 0.585
0.00016 M

Let’s test more combinations

Group	Fe^{3+} 0.00200 M	SCN^- 0.00200 M	*Abs*	K_c
Kate+Elijah	9	1	0.163	
Harper+Sierra	6	4	0.424	160
Jason+Ezra	7	3	0.370	160
Aviya+Stella	3	7	0.440	195
Brigitte+Natalie	2	8	0.395	255
Benjamin+Bobby	8	2	0.278	157
Rosie+Esther	4	6	0.460	188
Jonah+Duggie	5	5	0.455	167

- Each group will pick a different combination

Let’s test more combinations

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- Each group will pick a different combination

Using Q to indicate the direction the reaction will proceed to reach equilibrium.

Practice F1
Pop Bead Model

Looking at your 3 Q values, compared to K = 9, and considering each corresponding shift direction, what can you conclude?

1. When *K* is > than Q, the reaction shifts left
2. When *K* is > than Q, the reaction shifts right
3. When *K* is < than Q, the reaction shifts left
4. When *K* is < than Q, the reaction shifts right
5. When *K* is = to Q, the reaction can shift in either direction.
6. When *K* is = to Q, the reaction wouldn’t shift at all.

Looking at your 3 Q values, compared to K = 9, and considering each corresponding shift direction, what can you conclude?

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4. When *K* is < than Q, the reaction shifts right
5. When *K* is = to Q, the reaction can shift in either direction.
6. When *K* is = to Q, the reaction wouldn’t shift at all.

Reaction Quotient, Q

- When given values that may NOT be at equilibrium, you can substitute them into the equilibrium expression to solve for Q
- If $K_{eq} = Q$ then you know those values are actually at equilibrium.
- If $K_{eq} > Q$ the right side is too large and the system will shift to the right to reach equilibrium.
- If $K_{eq} < Q$ the right side is too small and the system will shift to the left to reach equilibrium.

$N_2O_{4(g)} \rightleftarrows 2NO_{2(g)}$ $K_c = 0.21$ at 100.ºC

At some point during the reaction at 100ºC,

$[N_2O_4] = 0.12$ M and $[NO_2] = 0.55$ M.

Is the reaction at equilibrium?

If not, in which direction is it progressing?

1. At equilibrium
2. Not at equilibrium, shift to the right.
3. Not at equilibrium, shift to the left.

→

$N_2O_{4(g)} \rightleftarrows 2NO_{2(g)}$ $K_c = 0.21$ at 100ºC

At some point during the reaction,

$[N_2O_4] = 0.12$ M and $[NO_2] = 0.55$ M.

Is the reaction at equilibrium? No

If not, in which direction is it progressing?

$$Q = \frac{[NO_2]^2}{[N_2O_4]} \qquad Q = \frac{[0.55]^2}{[0.12]} = 2.5$$

1. At equilibrium
2. Not at equilibrium, shift to the right.
3. Not at equilibrium, shift to the left.

$0.21 < 2.5$

$K < Q$

- K < Q, thus the reaction will proceed to the left.

→

Using Equilibrium Constants to Calculate Equilibrium Concentrations

For the reaction shown below, the

K_{eq} = 1.45 x 10^{-5}.

In an equilibrium mixture of the three gases at 500ºC, the partial pressure of

H_2 = 0.928 atm, and N_2 = 0.432 atm.

Calculate the equilibrium pressure of NH_3.

$$2\ NH_{3(g)} \quad \leftrightarrows \quad N_{2(g)} \quad + \quad 3\ H_{2(g)}$$

For the reaction shown below, the $K_{eq} = 1.45 \times 10^{-5}$.

In an equilibrium mixture of the three gases at 500ºC, the partial pressure of H_2 = 0.928 atm, and N_2 = 0.432 atm. Calculate the equilibrium pressure of NH_3.

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

- Not all problems require that you use a RICE box.
- Write the equilibrium expression.

$$K_p = \frac{(P_{H_2})^3(P_{N_2})}{(P_{NH_3})^2}$$

- Plug in the known equilibrium values and solve for the NH_3 pressure.

$$1.45 \times 10^{-5} = \frac{(0.928)^3(0.432)}{(P_{NH_3})^2} \qquad P_{NH_3} = 154 atm$$

→

- Consider the hypothetical reaction:
- $A_{(g)} + B_{(g)} \leftrightharpoons 2C_{(g)}$ for which $K_p = 4$

- Suppose 2 atm of each substance was placed in a 1 L container, is the system at equilibrium?

- If not, what is the pressure of each substance at equilibrium

- Consider the hypothetical reaction:
- $A_{(g)} + B_{(g)} \leftrightarrows 2C_{(g)}$ for which $K_p = 4$
- Suppose 2 atm of each substance was placed in a 1 L container, is the system at equilibrium? No
- What is the pressure of each substance at equilibrium
- Write the equilibrium expression.

$$K = \frac{(P_C)^2}{(P_A)(P_B)}$$

- Put in initial values and solve for Q, compare Q to K_{eq} to determine the direction of the shift. $K_p > Q$ thus shift right
- Use x to name the changes
- Put in equilibrium values using x

$$\frac{(2+2x)^2}{(2-x)^2} = 4$$

Look for the easy solve:square root both sides

$$\frac{(2+2x)}{(2-x)} = 2$$

- Solve.

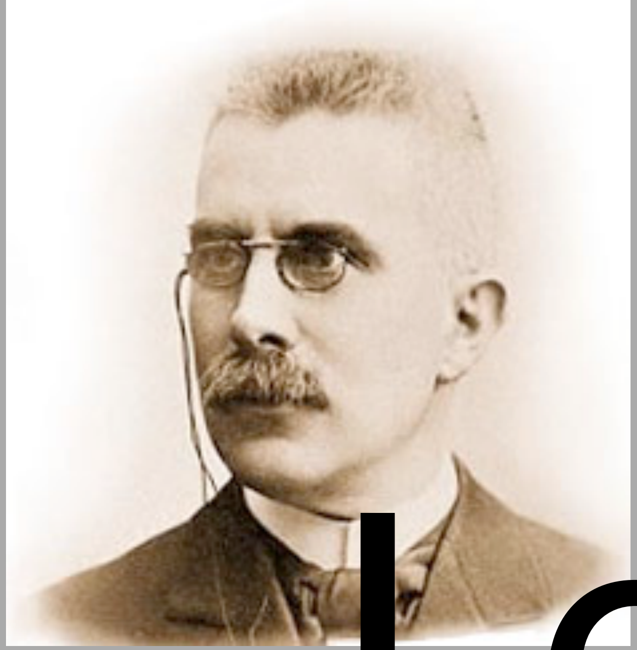
R	A +	B $\leftrightarrows$	2 C
I	2	2	2
C	− x	− x	+ 2x
E	2 − x	2 − x	2 + 2x

$$(2+2x) = 2(2-x)$$

x = 0.5

Be sure and answer the question:

A = B = 1.5
C = 3



Equi ⇆ librium

LeChâtelier's Principle

When a chemical system at equilibrium is disturbed, the system shifts in a direction to counteract that disturbance.

A system will always act to oppose changes in equilibrium

LeChatelier’s Principle

A general rule that will help us predict the direction in which an equilibrium reaction will move when the equilibrium is disturbed.

If an external “stress” is applied to a system at equilibrium, the system adjusts in such a way that the “stress” is partially offset as the system reaches a new equilibrium position.

Consider the gas phase reaction

$A \leftrightharpoons 2B$ endothermic $K = 0.2$

- Suppose we are at equilibrium with A = 5 M and B = 1 M
- If 5 M of A were added, how would the system respond?

1. Shift right, no change K
2. Shift left, no change in K
3. No shift, no change in K
4. Shift right, K becomes a larger value
5. Shift left, K becomes a smaller value

Consider the gas phase reaction
$A \leftrightharpoons 2B$ endothermic $K = 0.2$

- If 5 M of A were added, how would the system respond?

1. Shift right, no change K

$$A \leftrightharpoons 2B$$

Extra A comes in, the system will respond by reacting in the forward direction, using up some of the A and producing more B until an new equilibrium position is reached.

Shift to the right, same K value.

Consider the gas phase reaction $A \leftrightharpoons 2B$ endothermic K = 0.2

- Suppose we are at equilibrium with A = 5 M and B = 1 M

$$K = \frac{[1]^2}{[5]} = 0.2$$

- If 5 M of A were added, how would the system respond?

$$Q = \frac{[1]^2}{[10]} = 0.1$$

$$K > Q$$

Thus, a shift to the right.

- The reaction would no longer be at equilibrium and would proceed to “relieve” the stress, and get back to equilibrium.
- The forward reaction would occur enough to make the amount of B larger while the amount of A smaller until equilibrium was restored.

$$\frac{[1+2x]^2}{[10-x]} = 0.2 \qquad x = 0.2$$

$$thus \quad A = 9.8, \; B = 1.4$$

Note that solving this equation requires the quadratic equation. AP will never put you in a situation in which you must use the quadratic to get an answer.

- We would call this a “shift in the equilibrium position” to the right.

$$K = \frac{[1.4]^2}{[9.8]} = 0.2$$

Consider the gas phase reaction $A \leftrightharpoons 2B$ endothermic $K_c = 0.2$

- Suppose we are at equilibrium with A = 5 M and B = 1 M
- If the container were compressed, (and remains at a constant temperature), from 2 L to 1 L, how would the system respond?

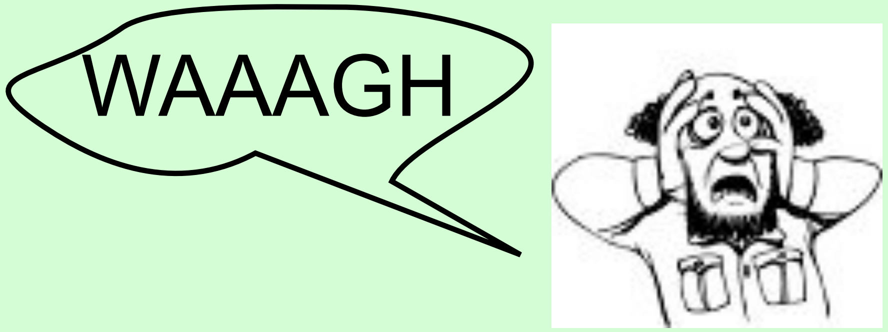
1. Shift right, no change K
2. Shift left, no change in K
3. No shift, no change in K
4. Shift right, K becomes a larger value
5. Shift left, K becomes a smaller value

Consider the gas phase reaction
$A \rightleftharpoons 2B$ endothermic $K_c = 0.2$

- If the container were compressed from 2 L to 1 L, how would the system respond?

2. Shift left, no change in K

$A \rightleftharpoons 2B$



Container is squashed, partial pressure of each gas increases, the system will respond by reacting in the reverse direction, using up some of the B and producing A until a new equilibrium position is reached.
Shift to the left, same K value.

Consider the gas phase reaction $A \rightleftharpoons 2B$ endothermic $K = 0.2$

- Suppose we are at equilibrium with A = 5 M and B = 1 M
- If the container were compressed from 2 L to 1 L, how would the system respond?
- The decrease in volume would double the molarity of each substance and the reaction would no longer be at equilibrium and would proceed to "relieve" the stress, and get back to equilibrium.
- The reverse reaction would occur to reduce the quantity of B and increase the quantity of A until equilibrium is restored.
- We would call this a "shift" to the left.
- Note that the new equilibrium position does not "get back to" A=1 nor B = 5.

$$K = \frac{[1]^2}{[5]} = 0.2$$

$$Q = \frac{[2]^2}{[10]} = 0.4$$

$$K < Q$$

Thus, a shift to the left.

$$\frac{[2-2x]^2}{[10+x]} = 0.2 \qquad x = 0.283$$

$$thus \quad A = 10.283, \quad B = 1.434$$

Note that solving this equation requires the quadratic equation. AP will never put you in a situation in which you must use the quadratic to get an answer.

$$K = \frac{[1.434]^2}{[10.283]} = 0.2$$

Consider the gas phase reaction $A \leftrightharpoons 2B$ endothermic $K = 0.2$

- Suppose we are at equilibrium with A = 5 M and B = 1 M
- If half of the amount of B were removed, how would the system respond?

1. Shift right, no change K
2. Shift left, no change in K
3. No shift, no change in K
4. Shift right, K becomes a larger value
5. Shift left, K becomes a smaller value

Consider the gas phase reaction $A \leftrightharpoons 2B$ endothermic $K = 0.2$

- If half of the amount of B were removed, how would the system respond?

1. Shift right, no change K

$A \leftrightharpoons 2B$

B is removed, the system will respond by reacting in the forward direction, using up some of the A and producing more B until an new equilibrium position is reached.
Shift to the right, same K value.

Consider the gas phase reaction $A \leftrightharpoons 2B$ endothermic K = 0.2

- Suppose we are at equilibrium with A = 5 M and B = 1 M

$$K = \frac{[1]^2}{[5]} = 0.2$$

- If half of the amount of B were removed, how would the system respond?

$$Q = \frac{[0.5]^2}{[5]} = 0.05$$

$$K > Q$$

Thus, a shift to the right.

- The decrease in B would cause the reaction to no longer be at equilibrium and would proceed to "relieve" the stress, and get back to equilibrium by shifting to try to restore some of that B.

$$\frac{[0.5+2x]^2}{[5-x]} = 0.2 \qquad x = 0.238$$

$$thus \quad A = 4.762, \quad B = 0.976$$

Note that solving this equation requires the quadratic equation. AP will never put you in a situation in which you must use the quadratic to get an answer.

- The forward reaction would occur to increase the quantity of B and decrease the quantity of A until equilibrium is restored.
- We would call this a "shift" to the right.

$$K = \frac{[0.976]^2}{4.762} = 0.2$$

Consider the gas phase reaction $A \leftrightharpoons 2B$ endothermic $K = 0.2$

- Suppose we are at equilibrium with A = 5 M and B = 1 M
- If the reaction vessel in the room was placed in an ice water bath, how would the system respond?

1. Shift right, no change K
2. Shift left, no change in K
3. No shift, no change in K
4. Shift right, K becomes a larger value
5. Shift left, K becomes a smaller value

Consider the gas phase reaction
$A \leftrightharpoons 2B$ endothermic $K = 0.2$

- If the reaction vessel were placed in an ice water bath, how would the system respond?

5. Shift left, K becomes a smaller value

$A \leftrightharpoons 2B$

Heat is removed, since the reaction is endothermic, the system will respond by reacting in the reverse direction, to produce more heat, using up some of the B and producing more A until an new equilibrium is reached.
Shift to the left, smaller K value.

Consider the gas phase reaction

Energy + A $\leftrightharpoons$ 2B endothermic K = 0.2

- Suppose we are at equilibrium with A = 5 M and B = 1 M
- If the reaction vessel were placed in an ice water bath, how would the system respond?
- We can "cheat" by considering the heat as a component of the reaction on the left due to the + sign of ΔH.
- The ice bath will reduce the temperature of the system, so the reaction will shift to reduce the effect of this temp change.
- A shift to the left will cause the production of heat which will reduce the disturbance of the equilibrium temperature.
- In this case, since there is a temp change, a new equlibrium, smaller K value will be reestablished at the new temperature. *You will not be asked to solve for the new K value, it is not an easy conversion.*
- K is only constant for a particular temperature.

Consider the gas phase reaction in a rigid container

$A \leftrightharpoons 2B$ endothermic $K = 0.2$

- Suppose we are at equilibrium with A = 5 M and B = 1 M
- An inert gas such as He has been added holding temperature constant so the total pressure increases.

1. Shift right, no change K
2. Shift left, no change in K
3. No shift, no change in K
4. Shift right, K becomes a larger value
5. Shift left, K becomes a smaller value

Consider the gas phase reaction $A \leftrightharpoons 2B$ endothermic $K = 0.2$

- Suppose we are at equilibrium with A = 5 M and B = 1 M
- An inert gas such as N_2 has been added.

3. No shift, no change in K

$A \leftrightharpoons 2B$

Inert gas is added, the total pressure increases, however the partial pressure of each gas remains the same, the system does not need to respond. Thus there is NO shift, and same K value.

$$K = \frac{[1]}{[5]} = 0.2 \quad \textit{and still} \quad K = \frac{[1]}{[5]} = 0.2$$

Consider the gas phase reaction $R \leftrightharpoons P$ endothermic $K = 5$

- Suppose we are at equilibrium with R = 1 M and P = 5 M
- If the container were increased in size from 1 L to 2 L, how would the system respond? (and remains at a constant temperature)

1. Shift right, no change K
2. Shift left, no change in K
3. No shift, no change in K
4. Shift right, K becomes a larger value
5. Shift left, K becomes a smaller value

Consider the gas phase reaction
$R \leftrightharpoons P$ endothermic $K = 5$

- Suppose we are at equilibrium with M = 1 M and P = 5 M
- If the container were increased in size from 1 L to 2 L, how would the system respond? (and remains at a constant temperature)

3. No shift, no change in K

$M \leftrightharpoons P$

The partial pressure of each gas decreases, but no shift of the system produces any relief in the number of molecules.
Thus there is NO shift, and same K value.

Consider the gas phase reaction $R \leftrightharpoons P$ endothermic K = 5

- Suppose we are at equilibrium with R = 1 M and P = 5 M

$$K = \frac{[5]}{[1]} = 5$$

- If the container were increased in size from 1 L to 2 L, how would the system respond?
- The concentrations would be cut in half, but since there is not stoichiometry to produce any exponents, the change in concentration occurs proportionately and Q = K

$$Q = \frac{[2.5]}{[0.5]} = 5$$

$$Q = K$$

- Thus the system is still at equilibrium, and there is no shift.

Thus, still at equilibrium.

LeChâtelier's Principle

- If *stress* is added to a system at equilibrium, the system will shift to relieve that stress.
- Types of stress:
  - ✦ Temperature (will also result in a different K_{eq}).
  - ✦ Adding or removing reactants or products.
    - ✓ Formation of precipitate removes reacting ions
  - ✦ Volume changes (affects only gases)
- Addition of a catalyst will change the rate at which equilibrium is achieved, but will *not* affect the equilibrium position.
- Addition of a gas (inert, non-reacting) will *not* affect the equilibrium position.

Just How *Constant* is the Equilibrium K*onstant?*

- The constant does *vary* with temperature.
- It does *not* depend on the initial amounts of reactants or products.
- It is *not* affected by the presence of any other materials, *not even a catalyst*.
- Equilibrium can be reached from either the forward or reverse directions.

Distinguish Equilibrium *Konstant from* Equilibrium *Position*

- For a particular temperature, there is only *one equilibrium constant*.
- But there are an *infinite* number of sets of various equilibrium concentrations, resulting in *many equilibrium positions*.

$PCl_{5(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)} \quad \Delta H = +87.9\ kJ$

- For the reaction above, in which direction will the reaction shift when $Cl_{2(g)}$ is removed

1. shift left (reactants favored)
2. shift right (the forward reaction is preferred)
3. no change

$PCl_{5(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)} \quad \Delta H = +87.9\ kJ$

- For the reaction above, in which direction will the reaction shift when $Cl_{2(g)}$ is removed

1. shift left
2. shift right
3. no change

$PCl_{5(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)}$ $\Delta H = +87.9$ kJ

- For the reaction above at equilibrium, in which direction will the reaction shift when the volume of the system is increased?

1. shift left
2. shift right
3. no change

$PCl_{5(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)} \quad \Delta H = +87.9\ kJ$

- For the reaction above, in which direction will the reaction shift when the volume of the system is increased?

1. shift left
2. shift right
    - The volume increase will cause an immediate decrease in pressure and the attempt to make up this pressure change will cause a shift toward more molecules = right
3. no change

Consider this reaction at equilibrium:

$$A_{(g)} \leftrightharpoons B_{(g)} + C_{(g)} + \text{energy}$$

In a 1 L container at equilibrium, the partial pressure of B is 2 atm, C is 2 atm and A is 2 atm.

$$K_p = \frac{(B)(C)}{(A)} = \frac{(2)(2)}{(2)} = 2$$

- If the container were expanded to 2 L the partial pressure of each gas would decrease to 1 atm (using PV = PV)

$$Q = \frac{(1)(1)}{(1)} = 1 < K_p \text{ thus shift right}$$

Consider this reaction at equilibrium:

$$A_{(g)} \rightleftharpoons B_{(g)} + C_{(g)} + \text{energy}$$

In a 1 L container at equilibrium, the partial pressure of B is 2 atm, C is 2 atm and A is 2 atm.

- What would the partial pressures be when the equilibrium position shifts to return the system back to equilibrium?

R	$A_{(g)}$	$\rightleftharpoons B_{(g)}$	$+ C_{(g)}$
I	1	1	1
C	$-x$	$+x$	$+x$
E	$1-x$	$1+x$	$1+x$
	0.764	1.236	1.236

$$K_p = 2 = \frac{(1+x)(1+x)}{(1-x)}$$

Using the quadratic − which you will NOT have to do for AP

$$x = 0.236 \text{ or } -4.24$$

$$K_p = \frac{(1.236)(1.236)}{(0.764)} = 1.9996!$$

$$PCl_{5(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)} \quad \Delta H = +87.9\ kJ$$

- For the reaction above, in which direction will the reaction shift when $PCl_{3(g)}$ is added in a sealed rigid container.

1. shift left
2. shift right
3. no change

$PCl_{5(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)} \quad \Delta H = +87.9\ \text{kJ}$

- For the reaction above, in which direction will the reaction shift when $PCl_{3(g)}$ is added

1. shift left
2. shift right
3. no change

Consider this reaction at equilibrium:

$$A_{(g)} \leftrightharpoons B_{(g)} + C_{(g)} + \text{energy}$$

In a 1 L container at equilibrium, the partial pressure of B is 2 atm, C is 2 atm and A is 2 atm.
B was added to the container making B = 4 atm

$$K_p = \frac{(B)(C)}{(A)} = \frac{(2)(2)}{(2)} = 2$$

- If more B were added to bring the total B pressure up to 4 atm,

$$Q = \frac{(4)(2)}{(2)} = 4 > K_p \text{ thus shift left}$$

Consider this reaction at equilibrium:

$$A_{(g)} \rightleftharpoons B_{(g)} + C_{(g)} + \text{energy}$$

In a 1 L container at equilibrium, the partial pressure of B is 2 atm, C is 2 atm and A is 2 atm.

B was added to the container making B = 4 atm

- What would the partial pressures be when the equilibrium position shifts to return the system back to equilibrium?

R	$A_{(g)} \rightleftharpoons B_{(g)} + C_{(g)}$		
I	2	4	2
C	$+x$	$-x$	$-x$
E	$2+x$	$4-x$	$2-x$
	2.536	3.464	1.464

$$K_p = 2 = \frac{(4-x)(2-x)}{(2+x)}$$

$$x = 0.536 \text{ or } 7.46$$

$$K_p = \frac{(3.464)(1.464)}{(2.536)} = 1.9997!$$

$PCl_{5(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)} \quad \Delta H = +87.9\ kJ$

- For the reaction above, in which direction will the reaction shift when the total pressure is increased by adding an inert gas, such as neon, into the reaction vessel?

1. shift left
2. shift right
3. no change

$$PCl_{5(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)} \quad \Delta H = +87.9\ kJ$$

- For the reaction above, in which direction will the reaction shift when the total pressure is increased by adding an inert gas such neon into the reaction vessel?

1. shift left
2. shift right
3. no change

- the total pressure changes, but the individual partial pressures of the gases do not change, so there is no shift in the equilibrium position.

Consider this reaction at equilibrium:

$$A_{(g)} \leftrightharpoons B_{(g)} + C_{(g)} + \text{energy}$$

In a 1 L container at equilibrium, the partial pressure of B is 2 atm, C is 2 atm and A is 2 atm.

$$K_p = \frac{(B)(C)}{(A)} = \frac{(2)(2)}{(2)} = 2$$

- If an inert gas is added, the total pressure increased, but no gas' partial pressure changed

$$Q = \frac{(2)(2)}{(2)} = 2 = K_p \text{ thus no change}$$

$PCl_{5(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)} \quad \Delta H = +87.9\ kJ$

- For the reaction above at equilibrium, in which direction will the reaction shift when the temperature is decreased

1. shift left
2. shift right
3. no change

$PCl_{5(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)}$ $\Delta H = +87.9$ kJ

- For the reaction above, in which direction will the reaction shift when the temperature is decreased?

1. shift left

- You can assume that the thermodynamics play a larger role than the pressure effects, however I don't think AP will put you in this situation.

2. shift right
3. no change

$$A_{(s)} + 2B_{(g)} \leftrightarrows 3C_{(g)}$$

- Which direction will the reaction shift when the pressure is increased by reducing the volume?

1. shift left
2. shift right
3. no change

$$A_{(s)} + 2B_{(g)} \leftrightarrows 3C_{(g)}$$

- Which direction will the reaction shift when the pressure is increased?

1. shift left
2. shift right
3. no change

- You might think it would stay the same because the amounts of moles are the same on both sides, but only gases respond to pressure changes, and thus the reaction will shift left.

$A_{(s)} + 2B_{(g)} \leftrightarrows 3C_{(g)}$

- If K_{eq} is 3.5 at 600ºC and K_{eq} is 45 at 100ºC, is this reaction exothermic or endothermic?

1. exothermic
2. endothermic
3. No way to determine, since ΔH is not given.

$A_{(s)} + 2B_{(g)} \leftrightarrows 3C_{(g)}$

- If K_{eq} is 3.5 at 600ºC and 45 at 100ºC, is this reaction exothermic or endothermic?

1. exothermic
2. endothermic
3. No way to determine, since ΔH is not given.

$$A_{(s)} + 2B_{(g)} \leftrightarrows 3C_{(g)}$$

- When at equilibrium, which direction will the reaction shift if a bit more A is added to the reaction vessel?

1. shift left
2. shift right
3. no change

$A_{(s)} + 2B_{(g)} \leftrightarrows 3C_{(g)}$

- Which direction will the reaction shift if a small amount of A is added?

1. shift left
2. shift right
3. no change
    - If there is no change in volume of the space available to the gases due to the increase in A added, there will be no effect on equilibrium. AP will expect you to ignore any volume change, unless they make it clear.

$$A_{(s)} + 2B_{(g)} \leftrightarrows 3C_{(g)}$$

- If the system is at equilibrium, what will happen to the mass of A if more B is added to the reaction vessel?

1. increase A and K stays constant
2. increase A and K increases
3. increase A and K decreases
4. decrease A and K stays constant
5. decrease A and K increases
6. decrease A and K decreases
7. A stays the same as does K

$A_{(s)} + 2B_{(g)} \leftrightarrows 3C_{(g)}$

- What will happen to the mass of A if more B is added to the reaction vessel?

1. increase A and K stays constant
2. increase A and K increases
3. increase A and K decreases
4. decrease A and K stays constant
5. decrease A and K increases
6. decrease A and K decreases
7. A stays the same as does K

Consider this reaction at equilibrium:

$$A_{(g)} \leftrightharpoons 2\,B_{(g)} + C_{(g)} + \text{energy}$$

Which of the following changes to the system would cause the concentration of B to increase?

1. decrease the volume of the system while maintaining constant temp
2. increase the temperature of the system while maintaining constant volume
3. removing A
4. removing C
5. adding a homogeneous catalyst

Consider this reaction at equilibrium:

$$A_{(g)} \leftrightharpoons 2\,B_{(g)} + C_{(g)} + \text{energy}$$

Which of the following changes to the system would cause the concentration of B to increase?

1. decrease the volume of the system while maintaining constant temp
   - This decrease of volume will cause a shift left, but the decrease in volume also causes and increase in concentration... let’s take a closer look at an example.
2. increase the temperature of the system while maintaining constant volume
3. removing A
4. removing C
5. adding a catalyst

Consider this reaction at equilibrium:

$$A_{(g)} \leftrightharpoons 2\,B_{(g)} + C_{(g)} + \text{energy}$$

In a 5 L container that contains 15 moles of B, 5 moles of C and 5 moles of A.

- Calculate K_c

No Calculator

Consider this reaction at equilibrium:

$$A_{(g)} \leftrightharpoons 2\,B_{(g)} + C_{(g)} + \text{energy}$$

In a 5 L container that contains 15 moles of B, 5 moles of C and 5 moles of A.

- $K_c = 9$

$$9 = \frac{[3]^2[1]}{[1]}$$

- If the volume of the system was decreased to 1L, calculate Q
- Then set up an equation that would allow you to solve for the new equilibrium position concentrations.

Consider this reaction at equilibrium:

$$A_{(g)} \leftrightharpoons 2\,B_{(g)} + C_{(g)} + \text{energy}$$

In a 5 L container that contains 15 moles of B, 5 moles of C and 5 moles of A.

- If the volume of the system was decreased to 1L, set up an RICE box that would allow you to solve for the new equilibrium position concentrations.

$$K_c = \frac{[B]^2[C]}{[A]} = 9$$

Consider this reaction at equilibrium:

$$A_{(g)} \rightarrow 2\,B_{(g)} + C_{(g)} + \text{energy}$$

In a 5 L container that contains 15 moles of B, 5 moles of C and 5 moles of A. If the volume of the system was decreased to 1L, set up an equation that would allow you to solve for the new equilibrium position concentrations.

R	$A_{(g)} \leftrightharpoons 2B_{(g)} + C_{(g)}$		
I	5	15	5
C	$+x$	$-2x$	$-x$
E	$5+x$	$15-2x$	$5-x$
	8.67	7.66	1.33

$$9 = \frac{[15-2x]^2[5-x]}{[5+x]} \qquad x = 3.67$$

- Which results in [B] = 7.66, [C] = 1.33, and [A] = 8.67
- You see, while the concentrations increase dramatically upon the initial volume change, the shift will be to the left, but the concentrations of B and C will never get lower than the original 5 and 1 before the volume change.

$N_2O_4 \rightleftharpoons 2NO_2$

Equilibrium

$$N_2O_4 \rightleftharpoons 2NO_2$$

1. ΔH of this reaction, is +
2. ΔH of this reaction, is −
3. ΔH of this reaction, can not be determined from the demonstration

$\text{Energy} + N_2O_4 \rightleftharpoons NO_2$

1. ΔH of this reaction, as written, is +

- As heat is added from the outside, the reaction shifts to the right to remove that stress. Thus the reaction must be endothermic.

2. ΔH of this reaction, as written, is −

3. ΔH of this reaction, as written, can not be determined from the demonstration

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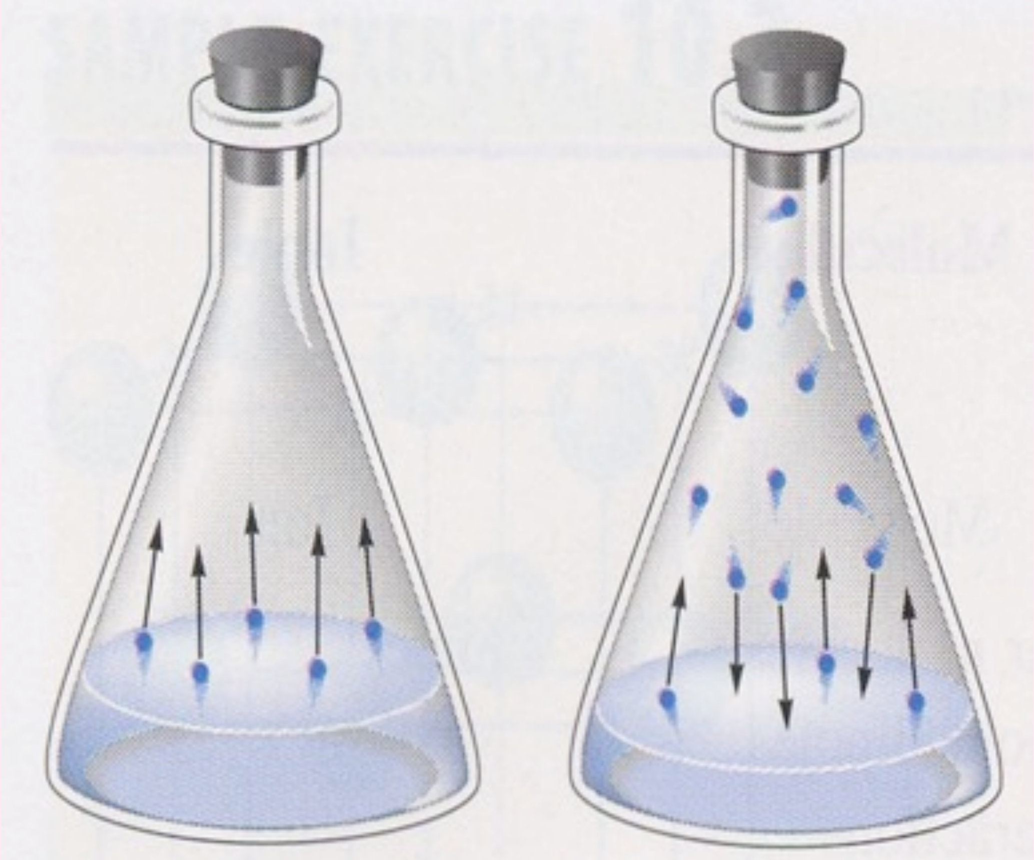
What speeds up when heat is added?

- $N_2O_4 + \text{Energy} \leftrightharpoons 2NO_2$
- When plunged into hot water, both the forward and reverse reactions will speed up because heat makes molecules move faster.
- Upon moving from cold to hot, initially, the forward reaction will speed up *more* than the reverse because the system is moving in a direction to use up the the external energy being applied, LeChatelier's Principle.
- As more NO_2 builds up, the reverse reaction speeds up more while the loss of N_2O_4 causes the forward reaction to slow down until the forward and reverse reactions are at the same rate *(albeit a faster rate than the previous equilibrium state)* and a new equilibrium position is established with a different, lower K value.

Equilibrium Situations

that you already know and love

- Vapor above a liquid in a *closed* container will reach equilibrium.
- The *rate of the condensation* and *rate of evaporation* will be equal.
- The amount of gas that can be evaporated at a particular temp is known as *equilibrium vapor pressure*.



Random Clicker Questions

For the reaction $A_{(g)} + B_{(g)} \leftrightharpoons C_{(g)} + D_{(g)}$
K was determined to be 0.5 at 500ºC
In an equilibrium mixture of these four gases at 500ºC, which one of the following is true?

1. [D] will always be greater than [B]
2. [D] will always be less than [B]
3. [D] will always be equal to [B]
4. [D] will never be equal to [B]
5. none of the above are true

For the reaction $A_{(g)} + B_{(g)} \leftrightharpoons C_{(g)} + D_{(g)}$
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4. [D] will never be equal to [B]
5. none of the above are true

Consider the reaction with $K_c = 2$ at 35ºC

$3A_{(g)} + 2B_{(s)} \leftrightharpoons 2C_{(g)}$ $\Delta H = +50$ kJ

1.0 mole of each substance is put into a 2.0 L container. *Select the true statement(s)* - No Calculators

1. The total pressure at equilibrium will be the same as the initial pressure.
2. The mass of B will be less at equilibrium than it was initially.
3. The temperature of the system will increase as it comes to equilibrium.
4. Addition of a catalyst will cause the partial pressure of C to increase.
5. Increasing the size of the container will cause the mass of A to increase.
6. None of the statements above are true.

Consider the reaction with $K_c = 2$ at 35ºC

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1. The total pressure at equilibrium will be the same as the initial pressure.
2. The mass of B will be less at equilibrium than it was initially.
3. The temperature of the system will increase as it comes to equilibrium.
4. Addition of a catalyst at equilibrium will cause the partial pressure of C to increase compared to the equilibrium pressure of C.
5. The rate of the forward reaction is initially greater than the rate of the reverse reaction.
6. None of the statements above are true.

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5. The rate of the forward reaction is initially greater than the rate of the reverse reaction.
6. None of the statements above are true.

Consider the reaction at some temperature.

$3A_{(g)} + 2B_{(s)} \leftrightharpoons 2C_{(g)}$ $\Delta H = +50$ kJ

Only C is put into a 1.0 L container.

Select the true statement(s).

1. At equilibrium the moles of C will equal the moles of B
2. At equilibrium, the moles of A > moles of B
3. The temperature of the system will increase as it comes to equilibrium.
4. At equilibrium, the total moles of A and B combined will be more than the moles of C.
5. Increasing the size of the container will cause K_c to decrease.
6. None of the statements above are true.

Consider the reaction at some temperature.

$3A_{(g)} + 2B_{(s)} \leftrightharpoons 2C_{(g)}$ $\Delta H = +50$ kJ

Only C is put into a 1.0 L container.

Select the true statement(s).

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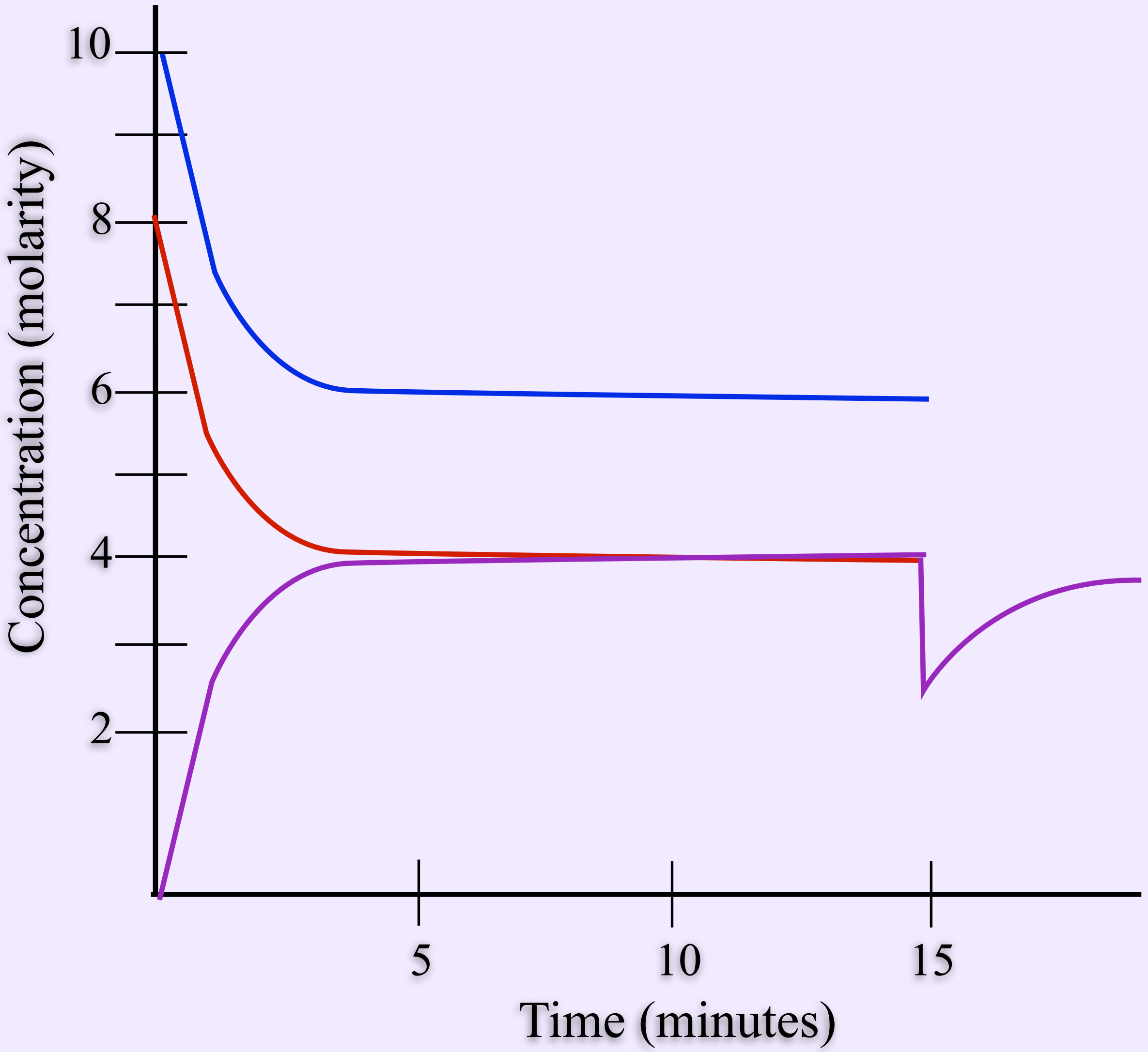
4. At equilibrium, the total moles of A and B combined will be more than the moles of C.
5. Increasing the size of the container will cause K_c to decrease.
6. None of the statements above are true.

For: $CO_{(g)} + Cl_{2(g)} \leftrightarrows COCl_{2(g)}$ + heat

A system in a sealed rigid container maintained at constant temperature is established in which the original concentration of CO is 10.0 M and that of Cl_2 is 8.0 M.

Which is the best comparison of Q, the reaction quotient, to K_c, the equilibrium constant, at time 1.5 minutes?

1. $Q > 1$ and $Q > K_c$
2. $Q > 1$ and $Q = K_c$
3. $Q > 1$ and $Q < K_c$
4. $Q < 1$ and $Q > K_c$
5. $Q < 1$ and $Q = K_c$
6. $Q < 1$ and $Q < K_c$



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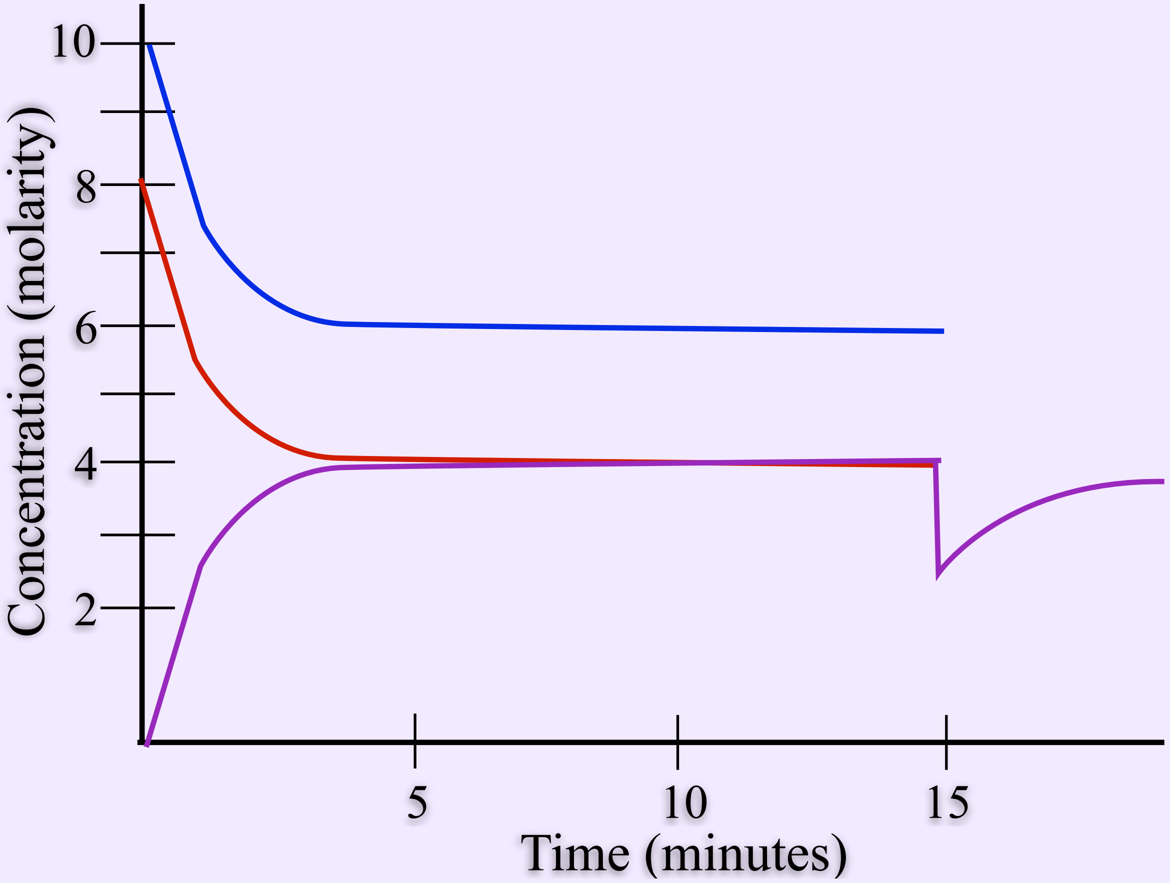
4. $Q < 1$ and $Q > K_c$
5. $Q < 1$ and $Q = K_c$
6. $Q < 1$ and $Q < K_c$

- Q is always positive, and we can see there are more reactants than products, and we know the reaction is moving forward since two chemicals are decreasing (must be the two reactants) and one chemical is increasing it must be the one product.

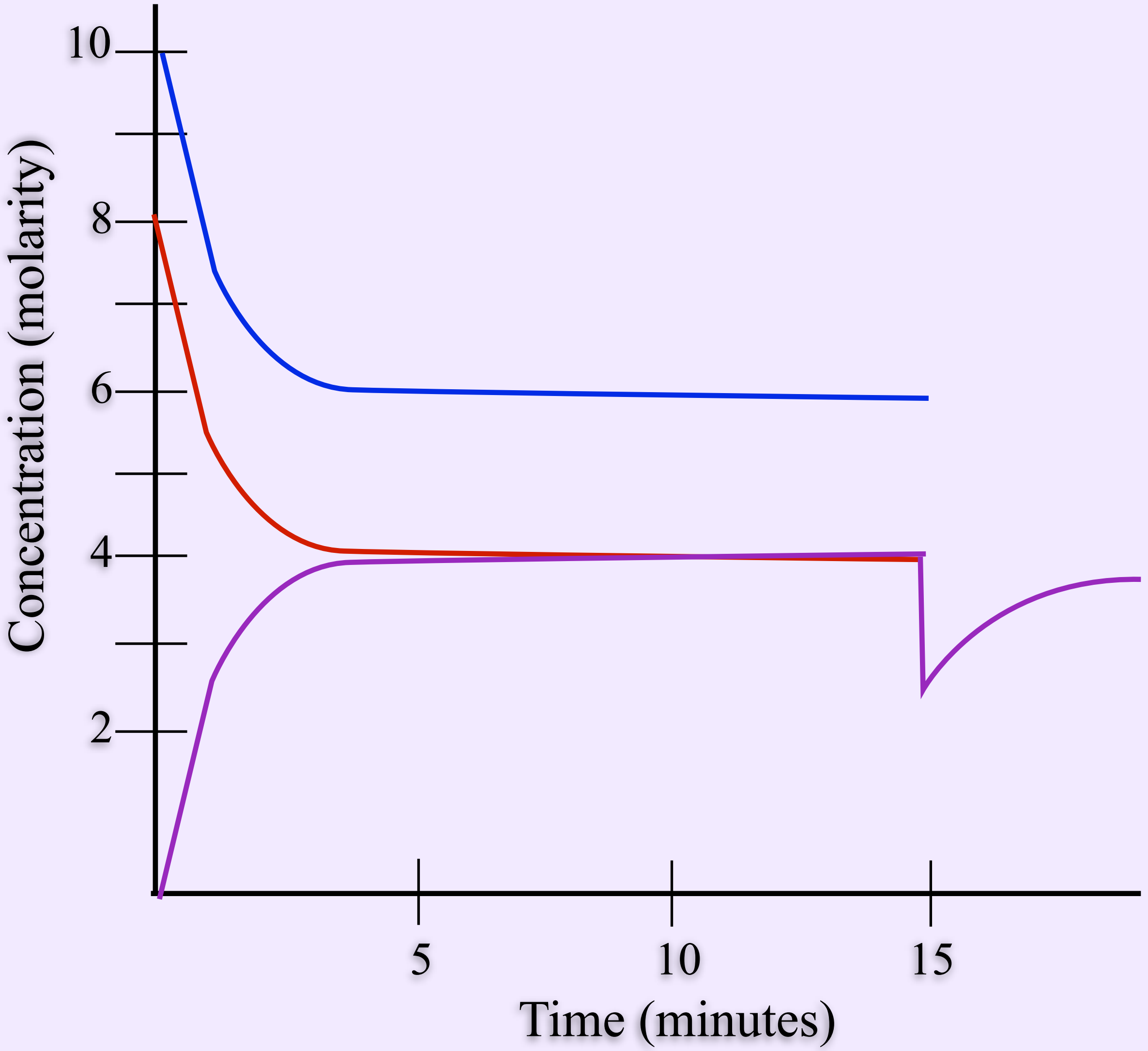


For: $CO_{(g)} + Cl_{2(g)} \leftrightarrows COCl_{2(g)}$ + heat

A system in a sealed rigid container maintained at constant temperature is established in which the original concentration of CO is 10.0 M and that of Cl_2 is 8.0 M.

Which is the best description of the rate of the forward reaction ($rate_{forward} = R_{fwd}$) between time 0 and time 4 minutes?

1. $R_{fwd} > R_{rvs}$ and R_{fwd} decreasing
2. $R_{fwd} > R_{rvs}$ and R_{fwd} increasing
3. $R_{fwd} = R_{rvs}$ and R_{fwd} constant
4. $R_{fwd} < R_{rvs}$ and R_{fwd} decreasing
5. $R_{fwd} < R_{rvs}$ and R_{fwd} increasing

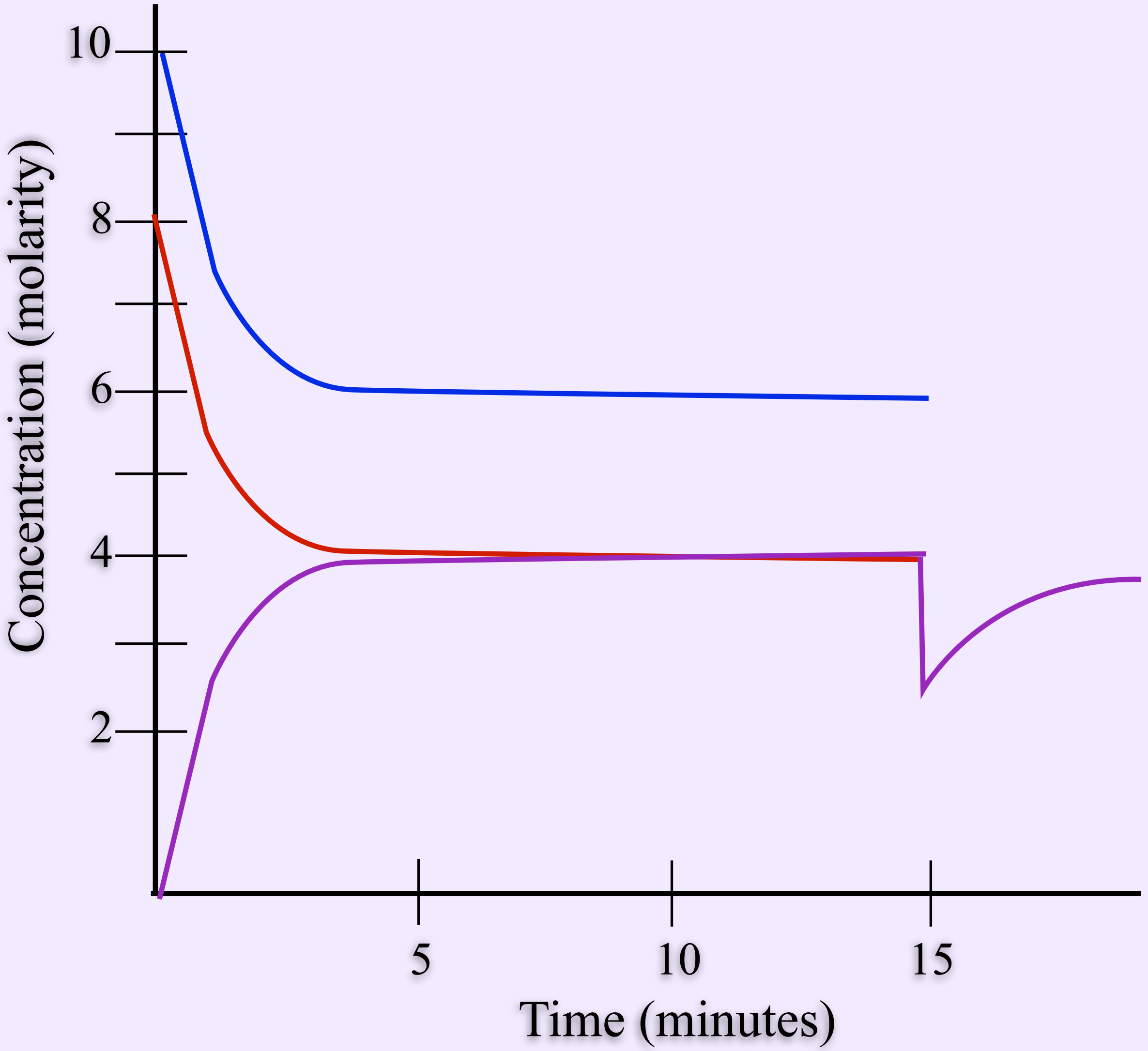


For: $CO_{(g)} + Cl_{2(g)} \leftrightarrows COCl_{2(g)}$ + heat

A system in a sealed rigid container maintained at constant temperature is established in which the original concentration of CO is 10.0 M and that of Cl_2 is 8.0 M.

Which is the best description of the rate of the forward reaction ($rate_{forward}$) between time 0 and time 4 minutes?

1. $R_{fwd} > R_{rvs}$ and R_{fwd} decreasing
2. $R_{fwd} > R_{rvs}$ and R_{fwd} increasing
3. $R_{fwd} = R_{rvs}$ and R_{fwd} constant
4. $R_{fwd} < R_{rvs}$ and R_{fwd} decreasing
5. $R_{fwd} < R_{rvs}$ and R_{fwd} increasing

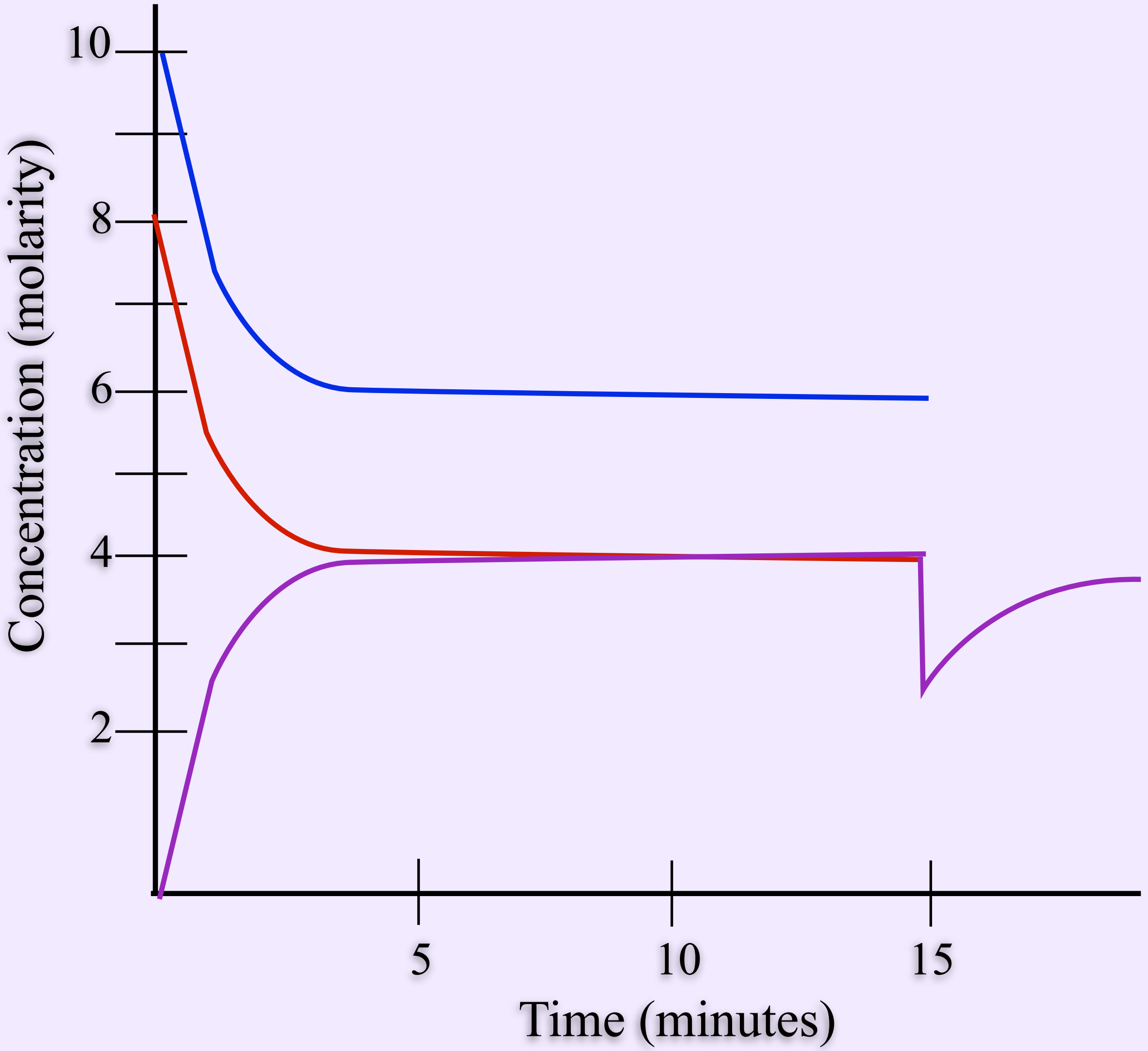


For: $CO_{(g)} + Cl_{2(g)} \leftrightarrows COCl_{2(g)}$ + heat

A system in a sealed rigid container maintained at constant temperature is established in which the original concentration of CO is 10.0 M and that of Cl_2 is 8.0 M.

Which is the best explanation of the cause of the changes in concentration that occur after 15 minutes?

1. increase in temperature
2. decrease in temperature
3. addition of a suitable catalyst
4. addition of $COCl_2$
5. removal of $COCl_2$



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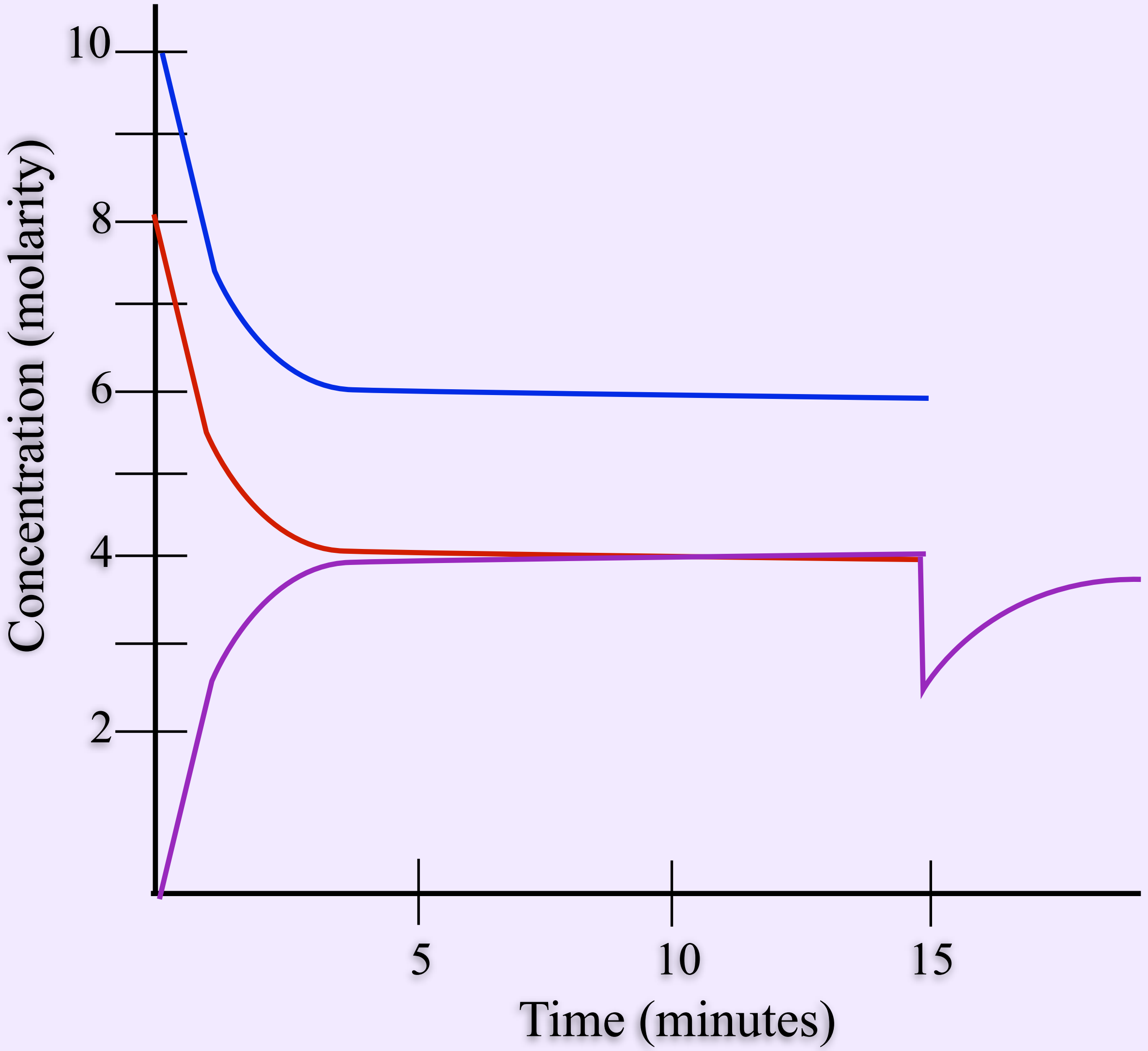


Which is the best comparison of the

- rate of the forward reaction at 10 min ($\text{rate}_{\text{forward,10 min}}$)

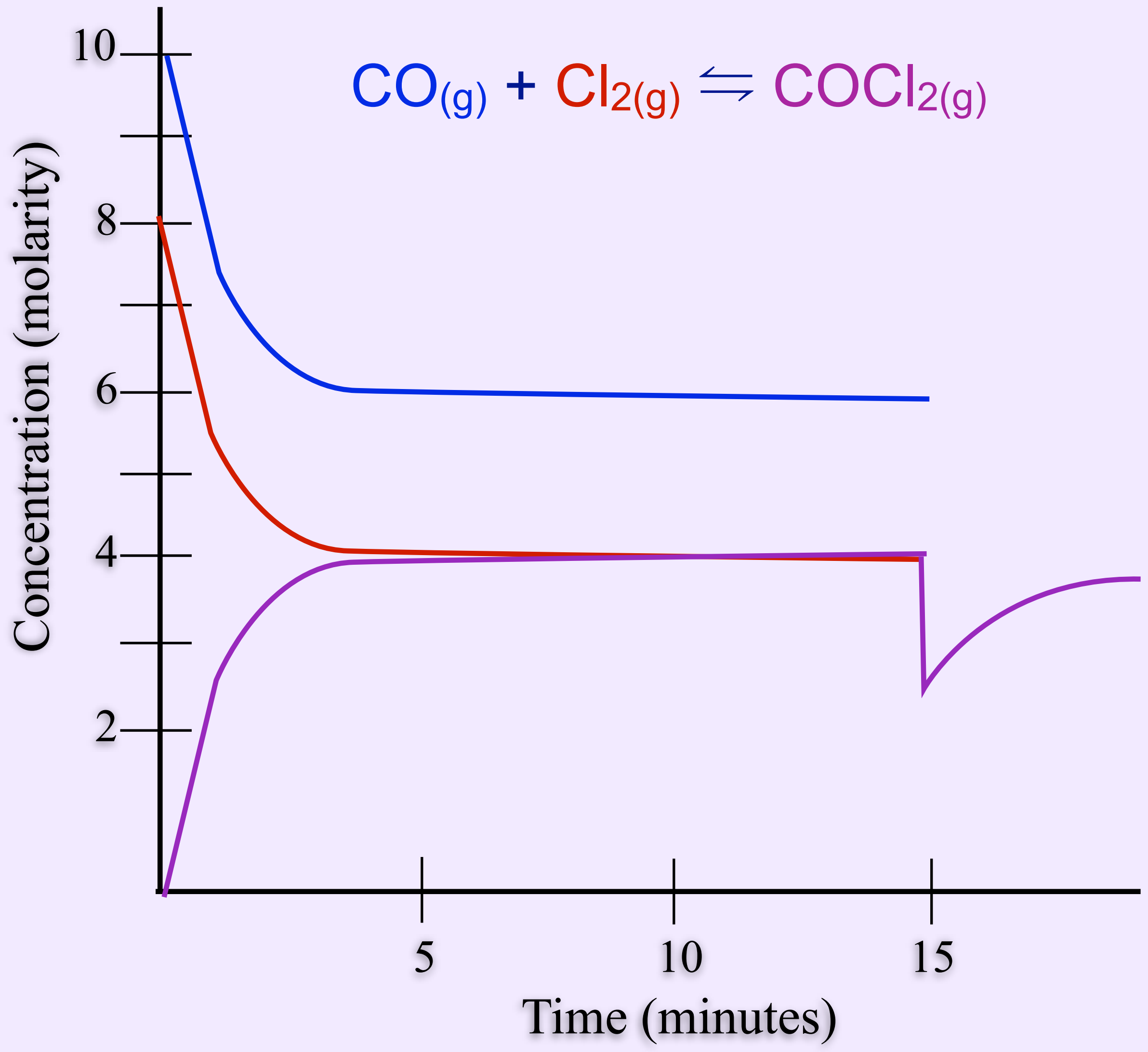
and the

- concentration of CO at 10 min ($[\text{CO}]_{\text{10 min}}$), the first equilibrium

to the

- corresponding characteristics at 20 minutes, when the second equilibrium is established

1. $R_{\text{fwd,10 min}} = R_{\text{fwd,20 min}}$;
   with $[\text{CO}]_{\text{10 min}} = [\text{CO}]_{\text{20 min}}$
2. $R_{\text{fwd,10 min}} < R_{\text{fwd,20 min}}$;
   with $[\text{CO}]_{\text{10 min}} = [\text{CO}]_{\text{20 min}}$
3. $R_{\text{fwd,10 min}} > R_{\text{fwd,20 min}}$;
   with $[\text{CO}]_{\text{10 min}} = [\text{CO}]_{\text{20 min}}$
4. $R_{\text{fwd,10 min}} < R_{\text{fwd,20 min}}$;
   with $[\text{CO}]_{\text{10 min}} > [\text{CO}]_{\text{20 min}}$
5. $R_{\text{fwd,10 min}} > R_{\text{fwd,20 min}}$;
   with $[\text{CO}]_{\text{10 min}} > [\text{CO}]_{\text{20 min}}$



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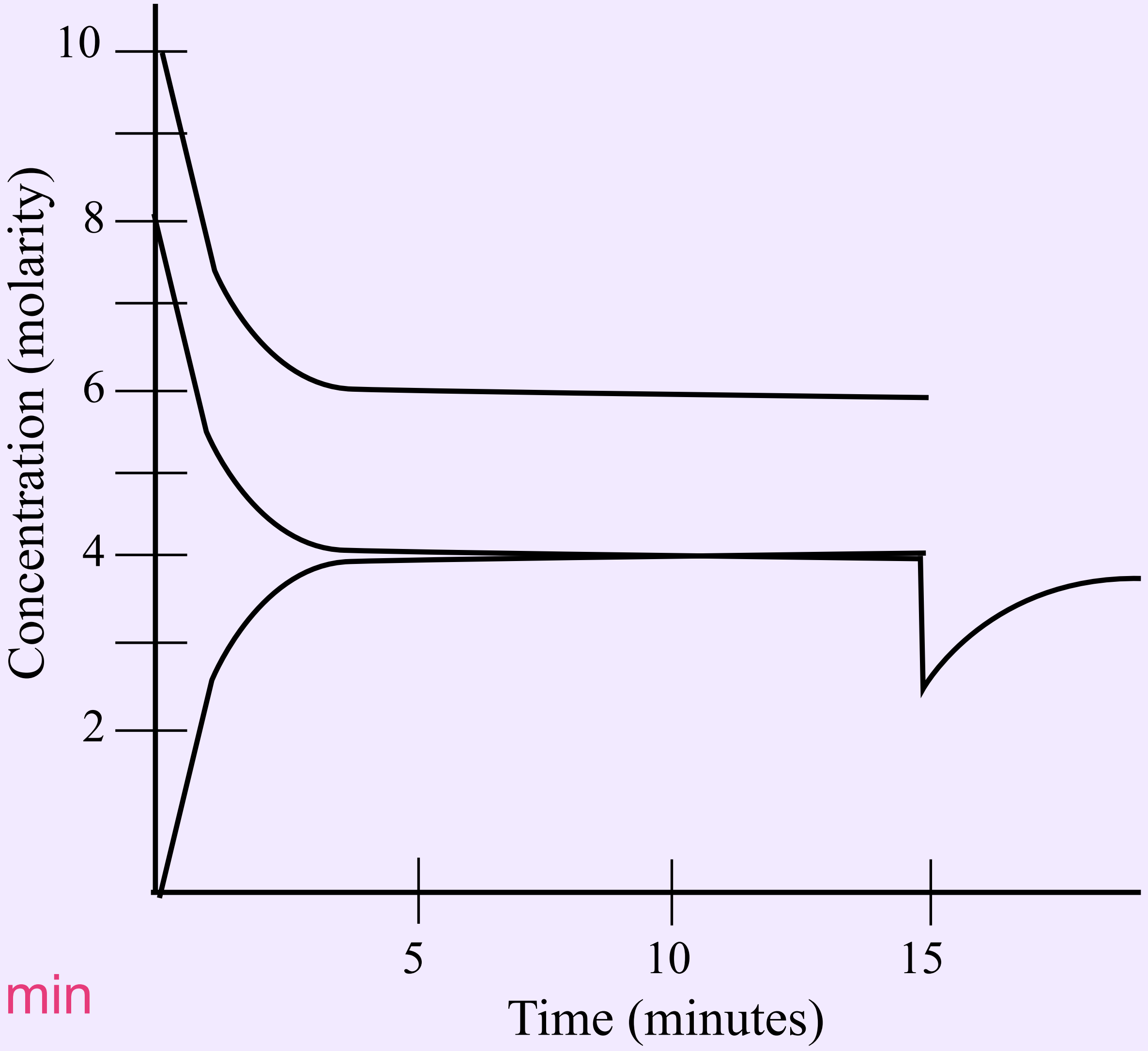
and the

- concentration of CO at 10 min ($[CO]_{10\text{ min}}$), the first equilibrium

to the

- corresponding characteristics at 20 minutes, when the second equilibrium is established

1. $\text{rate}_{\text{forward,10 min}} = \text{rate}_{\text{forward,20 min}}$; with $[CO]_{10\text{ min}} = [CO]_{20\text{ min}}$
2. $\text{rate}_{\text{forward,10 min}} < \text{rate}_{\text{forward,20 min}}$; with $[CO]_{10\text{ min}} = [CO]_{20\text{ min}}$
3. $\text{rate}_{\text{forward,10 min}} > \text{rate}_{\text{forward,20 min}}$; with $[CO]_{10\text{ min}} = [CO]_{20\text{ min}}$
4. $\text{rate}_{\text{forward,10 min}} < \text{rate}_{\text{forward,20 min}}$; with $[CO]_{10\text{ min}} > [CO]_{20\text{ min}}$
5. $\text{rate}_{\text{forward,10 min}} > \text{rate}_{\text{forward,20 min}}$; with $[CO]_{10\text{ min}} > [CO]_{20\text{ min}}$



For the reaction: $CaCO_{3(s)} \leftrightarrows CaO_{(s)} + CO_{2(g)}$

Which of the following initial situations are capable of reaching equilibrium? Select as many as apply

1. pure $CaCO_3$
2. some CaO and a pressure of CO_2 greater than the equilibrium (K_p) value
3. some CaO and a pressure of CO_2 less than the equilibrium (K_p) value
4. some $CaCO_3$ and a pressure of CO_2 greater than the equilibrium (K_p) value
5. some $CaCO_3$ and a pressure of CO_2 less than the equilibrium (K_p) value
6. $CaCO_3$ and CaO

For the reaction: $CaCO_{3(s)} \leftrightharpoons CaO_{(s)} + CO_{2(g)}$

Which of the following initial situations are capable of reaching equilibrium? Select as many as apply

1. pure $CaCO_3$
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5. some $CaCO_3$ and a pressure of CO_2 less than the equilibrium (K_p) value
6. $CaCO_3$ and CaO

Consider the following reaction.

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2\,HI_{(g)}$$

$$\Delta H = +25\ \text{kJ}$$

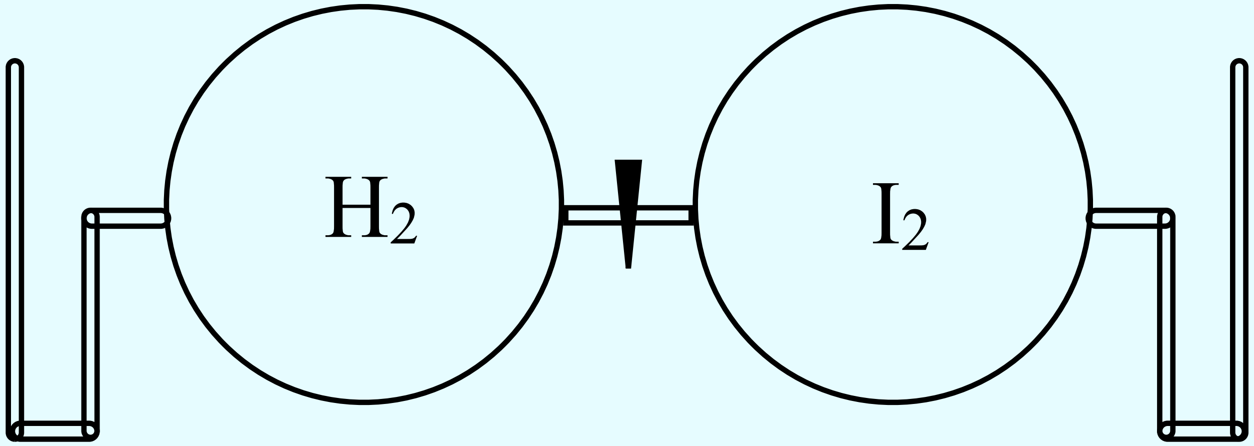
It there are equal quantities (moles) of the two gases, at the same temperature, before the stopcock is opened, what would you observe?

Select all that apply.

1. The color of the two gas bulbs are the same.
2. The manometers will be at the same height.
3. The kinetic energy of the two gases are the same.
4. The “average” speed of the two gases is the same.
5. None of the above are true.

$H_{2(g)} + I_{2(g)} \leftrightharpoons 2\,HI_{(g)}$

$\Delta H = +25\text{ kJ}$



It there are equal quantities (moles) of the two gases, at the same temperature, before the stopcock is opened, what would you observe (be true)? *Select all that apply.*

1. The color of the two gas bulbs are the same.
    - I_2 is purple, H_2 is colorless
2. The manometers will be at the same height.
    - With equal quantites that are at the same temp, they will exert equal pressure.
3. The kinetic energy of the two gases are the same.
    - Since the gases are at the same temp, they must have the same KE since $T \alpha \frac{1}{2}mv^2$
4. The "average" speed of the two gases is the same.
    - H_2 has a smaller MM, thus has a greater speed.
5. None of the above are true.

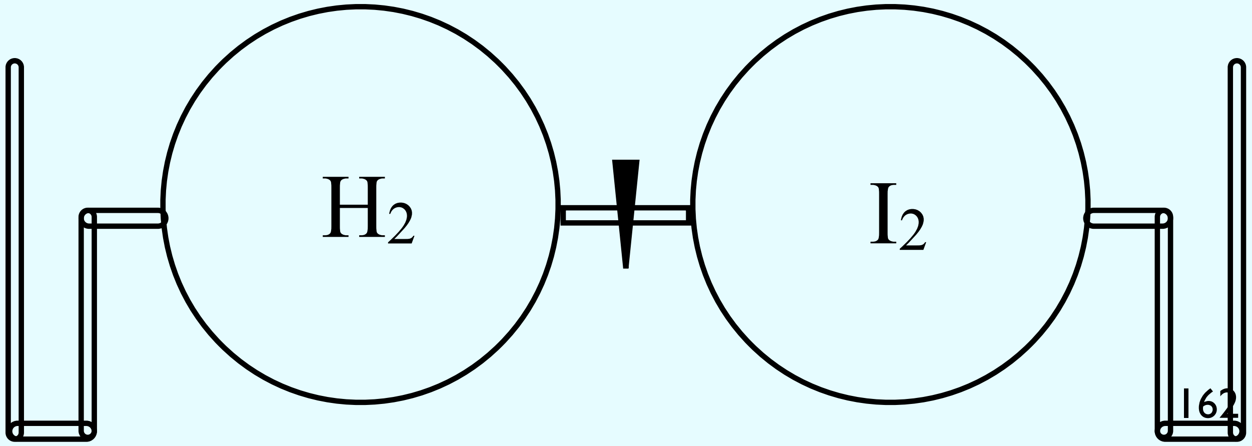
It the stopcock is opened, and equilibrium is established, what would you observe?

Select all that apply.

1. The color of the two gas bulbs are the same as each other.
2. The two manometers will be at the same height as each other.
3. The two manometers will be at the same height as they were before the stopcock was opened and equilibrium established.
4. The "average" speed of the H_2 is the same as it was before equlibrium was established.
5. None of the above are true.

$$H_{2(g)} + I_{2(g)} \leftrightarrows 2\,HI_{(g)}$$

$$\Delta H = +25\text{ kJ}$$



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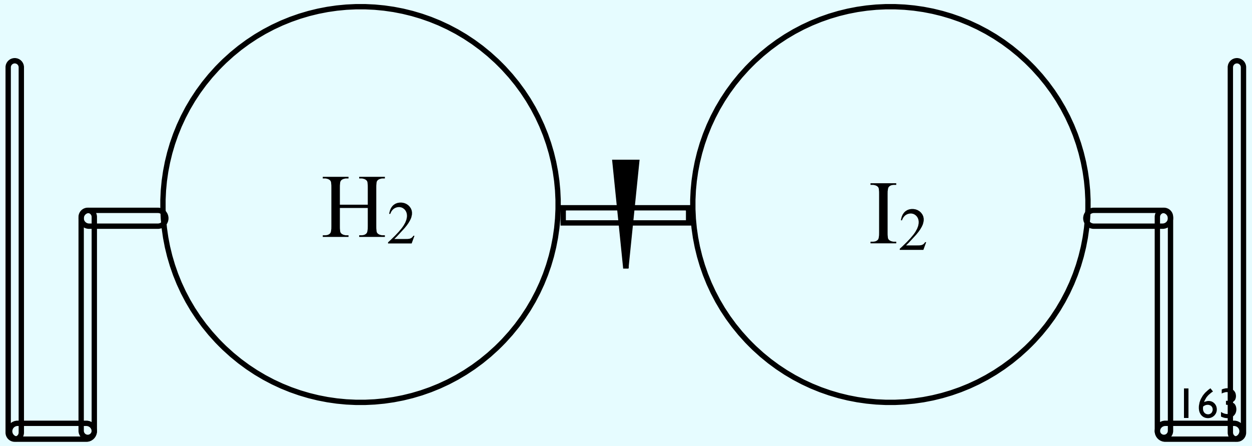
Select all that apply.

1. The color of the two gas bulbs are the same as each other.
2. The two manometers will be at the same height as each other.
3. The two manometers will be at the same height as they were before the stopcock was opened and equilibrium established.
4. The “average” speed of the H_2 is the same as it was before equlibrium was established.
    - In fact it would be slower as the temperature would have decreased since the formation of product is endothermic.
5. None of the above are true.

$$H_{2(g)} + I_{2(g)} \rightleftarrows 2\,HI_{(g)}$$

$$\Delta H = +25\text{ kJ}$$

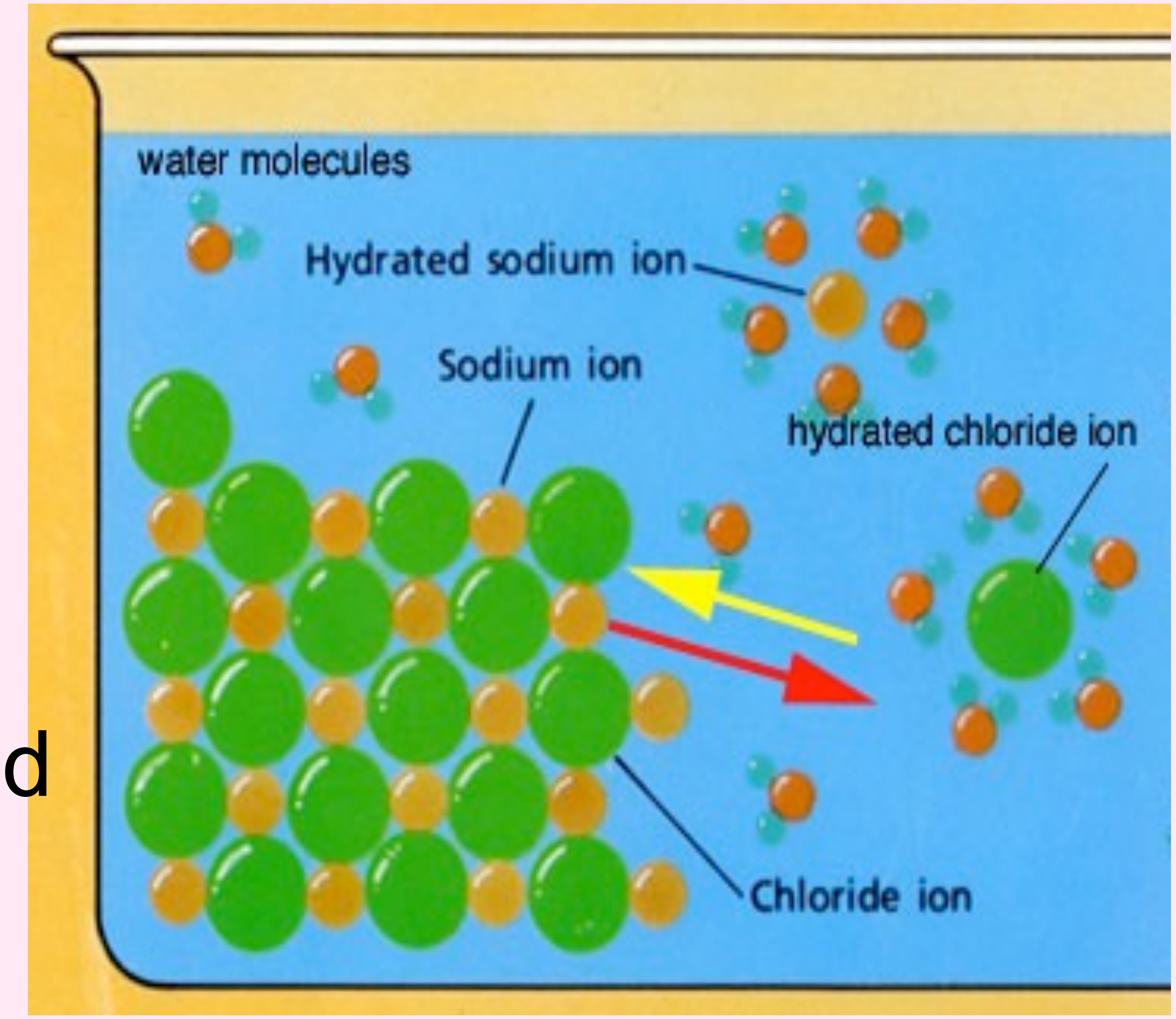


That’s all for now.

Equilibrium Situations

that you already know and love

- *Saturated solution*
  - ✓ A solution that contains as much dissolved solid as possible (at a given temperature) with some undissolved solid on the bottom.
- The *rate of the dissolution* (red arrow) and *rate of crystallization* (yellow arrow) will be *equal*.
- *Solubility* is the maximum quantity of solid that can be dissolved and exist in equilibrium at a particular temp.



Take a brief look at the Phet Demo

Calculating Equilibrium Concentrations

- Let’s stop and do problem # 10

10. Consider the reaction:

$2\ H_2S_{(g)} \leftrightharpoons 2\ H_{2(g)} + S_{2(g)}$ $K_p = 0.035$ at temperature, T

A reaction mixture contains 0.112 atm of H_2, 0.055 atm S_2 and 0.445 atm of H_2S. Is this reaction mixture at equilibrium? If not, in what direction will the reaction proceed? Calculate the partial pressure of each gas at equilibrium.

Calculating Equilibrium Concentrations

- Let's stop and do problem # 10

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Although AP will NEVER present a problem in which you would need the quadratic to solve the problem, WE can go ahead and solve this type of problem. Set up the RICE box and then the equilbrium equation, then use Wolfram Alpha to solve.

ANSWER $Q = 0.107$

$x = 0.047$

Calculating Equilibrium Concentrations

- Problem # 10 needs REVISIONS

$$K_p = \frac{\left(P_{H_2}\right)^2\left(P_{S_2}\right)}{\left(P_{H_2S}\right)^2}$$

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A reaction mixture contains 0.112 atm of H_2, 0.055 atm S_2 and 0.445 atm of H_2S. Is this reaction mixture at equilibrium? If not, in what direction will the reaction proceed? Calculate the partial pressure of each gas at equilibrium.

$$Q = \frac{(0.112)^2(0.055)}{(0.445)^2} = 0.0035 < K_p \text{ thus shift right}$$

$$K_p = \frac{(0.112+2x)^2(0.055+x)}{(0.445-2x)^2} = 0.035$$

R	$2\ H_2S \leftrightharpoons$	$2\ H_2$	$+\ S_2$
I	0.445	0.112	0.055
C	$+ 2x$	$- 2x$	$- x$
E	$0.445 - 2x$	$0.112 + 2x$	$0.055 + x$

Calculating Equilibrium Constants

- Let's stop and do problem # 5

5. Consider the reaction:
   $CO_{(g)} + 2\ H_{2(g)} \leftrightharpoons CH_3OH_{(g)}$

An equilibrium mixture of this reaction at a certain temperature was found to have $[CO] = 0.105$ M, $[H_2] = 0.114$ M, and $[CH_3OH] = 0.185$ M. What is the value of the equilibrium constant, K_c at this temperature?

Calculating Equilibrium Constants

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An equilibrium mixture of this reaction at a certain temperature was found to have [CO] = 0.105 M, $[H_2]$ = 0.114 M, and $[CH_3OH]$ = 0.185 M. What is the value of the equilibrium constant, K_c at this temperature?

$$K_c = \frac{[CH_3OH]}{[H_2]^2[CO]} \qquad K_c = \frac{[0.185]}{[0.114]^2[0.105]} \qquad K_c = 136$$

Calculating Equilibrium Constants

- Let’s stop and do problem # 6

6. Consider the reaction:

$$2\ CH_{4(g)} \leftrightharpoons C_2H_{2(g)} + 3\ H_{2(g)}$$

A reaction mixture at 1700ºC initially contains $[CH_4] = 0.115$ M. At equilibrium, the mixture contains $[C_2H_2] = 0.035$ M. What is the value of the equilibrium constant, K_c at this temperature?

Calculating Equilibrium Constants

- problem # 6 continued

6. Consider the reaction:

   $2\ CH_{4(g)} \leftrightharpoons C_2H_{2(g)} + 3\ H_{2(g)}$

A reaction mixture at 1700ºC initially contains $[CH_4] = 0.115$ M. At equilibrium, the mixture contains $[C_2H_2] = 0.035$ M. What is the value of the equilibrium constant, K_c at this temperature?
ANSWER $K_c = 0.020$

$$K_c = \frac{[C_2H_2][H_2]^3}{[CH_4]^2} \qquad K_c = \frac{[C_2H_2][H_2]^3}{[CH_4]^2}$$

Calculating Equilibrium Constants

- problem # 6 continued

6. Consider the reaction:

   $2\ CH_{4(g)} \leftrightharpoons C_2H_{2(g)} + 3\ H_{2(g)}$

A reaction mixture at 1700ºC initially contains $[CH_4] = 0.115$ M. At equilibrium, the mixture contains $[C_2H_2] = 0.035$ M. What is the value of the equilibrium constant, K_c at this temperature?
ANSWER $K_c = 0.020$

$$K_c = \frac{[C_2H_2][H_2]^3}{[CH_4]^2} \qquad K_c = \frac{[C_2H_2][H_2]^3}{[CH_4]^2}$$

Using Q to Determine Shift

- Let's stop and do problem # 7

7. Consider the reaction:

$I_{2(g)} + Cl_{2(g)} \leftrightharpoons 2\ ICl_{(g)} \quad K_p = 81.9$

A reaction mixture contains 0.100 atm of I_2, 0.100 atm Cl_2 and 0.445 atm of ICl. Is this reaction mixture at equilibrium? If not, in what direction will the reaction proceed? Calculate the partial pressure of each gas at equilibrium.

Using Q to Determine Shift

- problem # 7 continued….

$$Q = \frac{\left(P_{ICl}\right)^2}{\left(P_{I_2}\right)\left(P_{Cl_2}\right)}$$

7. Consider the reaction:
$I_{2(g)} + Cl_{2(g)} \leftrightharpoons 2\,ICl_{(g)} \quad K_p = 81.9$

A reaction mixture contains 0.100 atm of I_2, 0.100 atm Cl_2 and 0.445 atm of ICl. Is this reaction mixture at equilibrium? If not, in what direction will the reaction proceed?

$$Q = \frac{(0.445)^2}{(0.1)(0.1)} = 19.8 < 81.9 \text{ thus shift right}$$

$CO_{(g)} + H_2O_{(g)} \rightleftarrows CO_{2(g)} + H_{2(g)}$

for this reaction, $K_c = 1.56$ at 900 K

If 2.0 M CO and 1.0 M H_2O gases were placed in a 1 L flask at 900 K, what is the composition of the equilibrium mixture?

1. `

$CO_{(g)} + H_2O_{(g)} \rightleftarrows CO_{2(g)} + H_{2(g)}$

for this reaction, $K_c = 1.56$ at 900 K

If 2.0 M CO and 1.0 M H_2O gases were placed in a 125 ml flask at 900 K, what is the composition of the equilibrium mixture?

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]} \qquad 1.56 = \frac{x^2}{(2-x)(1-x)}$$

R	CO	+ H_2O	⇌ CO_2	+ H_2
I	2	1	0	0
C	− x	− x	+ x	+ x
E	2 − x	1 − x	x	x

Although AP will NEVER present a problem in which you would need the quadratic to solve the problem, WE can go ahead and solve this type of problem. Use a quatratic equation program to solve:

x = 7.6 or 0.73

but only one makes sense since subtracting 7.6 would cause a negative molarity.

Looking for ways to solve while avoiding the time drain of the quadratic.

Consider the reaction:

$$I_{2(g)} + Cl_{2(g)} \leftrightharpoons 2\ ICl_{(g)} \quad K_p = 81.9$$

A reaction mixture contains 0.100 atm of I_2, 0.100 atm Cl_2 and 0.445 atm of ICl. Since we know this reaction mixture must proceed to the right, we can calculate the partial pressure of each gas at equilibrium.

give it a try……set up the rice box, then the equilibrium expression….

Looking for ways to solve while avoiding the time drain of the quadratic.

- Let's work problem # 9 a bit further

$$K_p = \frac{[ICl]^2}{[I_2][Cl_2]}$$

9. Consider the reaction:
$I_{2(g)} + Cl_{2(g)} \leftrightharpoons 2\,ICl_{(g)} \quad K_p = 81.9$

A reaction mixture contains 0.100 atm of I_2, 0.100 atm Cl_2 and 0.445 atm of ICl. Since we know this reaction mixture must proceed to the right, we can calculate the partial pressure of each gas at equilibrium.

$$81.9 = \frac{[0.445 + x]^2}{[0.1 - x][0.1 - x]}$$

$$81.9 = \frac{[0.445 + x]^2}{[0.1 - x]^2}$$

$$\sqrt{81.9} = \sqrt{\frac{[0.445 + x]^2}{[0.1 - x]^2}}$$

$$9.05 = \frac{[0.445 + x]}{[0.1 - x]}$$

$$0.905 - 9.05x = 0.445 + x$$

$$0.46 = 10.05x$$

$$x = 0.0458$$

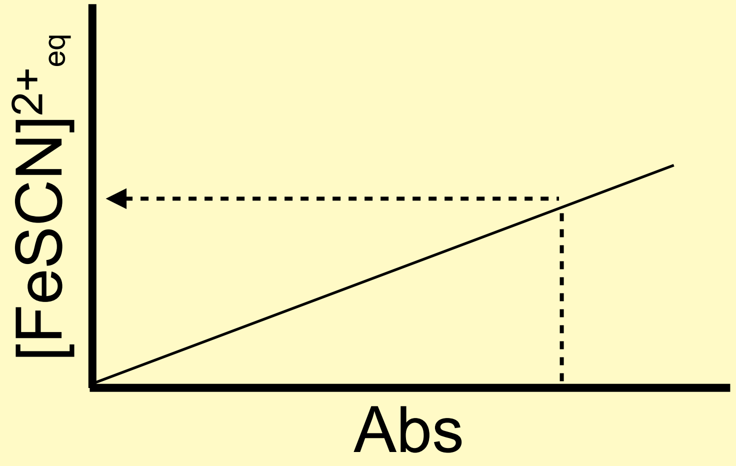
R	I_2 +	Cl_2	$\leftrightharpoons$ 2 ICl
I	0.1	0.1	0.445
C	− x	− x	+ x
E	0.1 − x	0.1 − x	0.445 + x
	0.054	0.054	0.491

During vacation, but before we returned to school this past Monday, I

(select only 1 that most applies to you.)

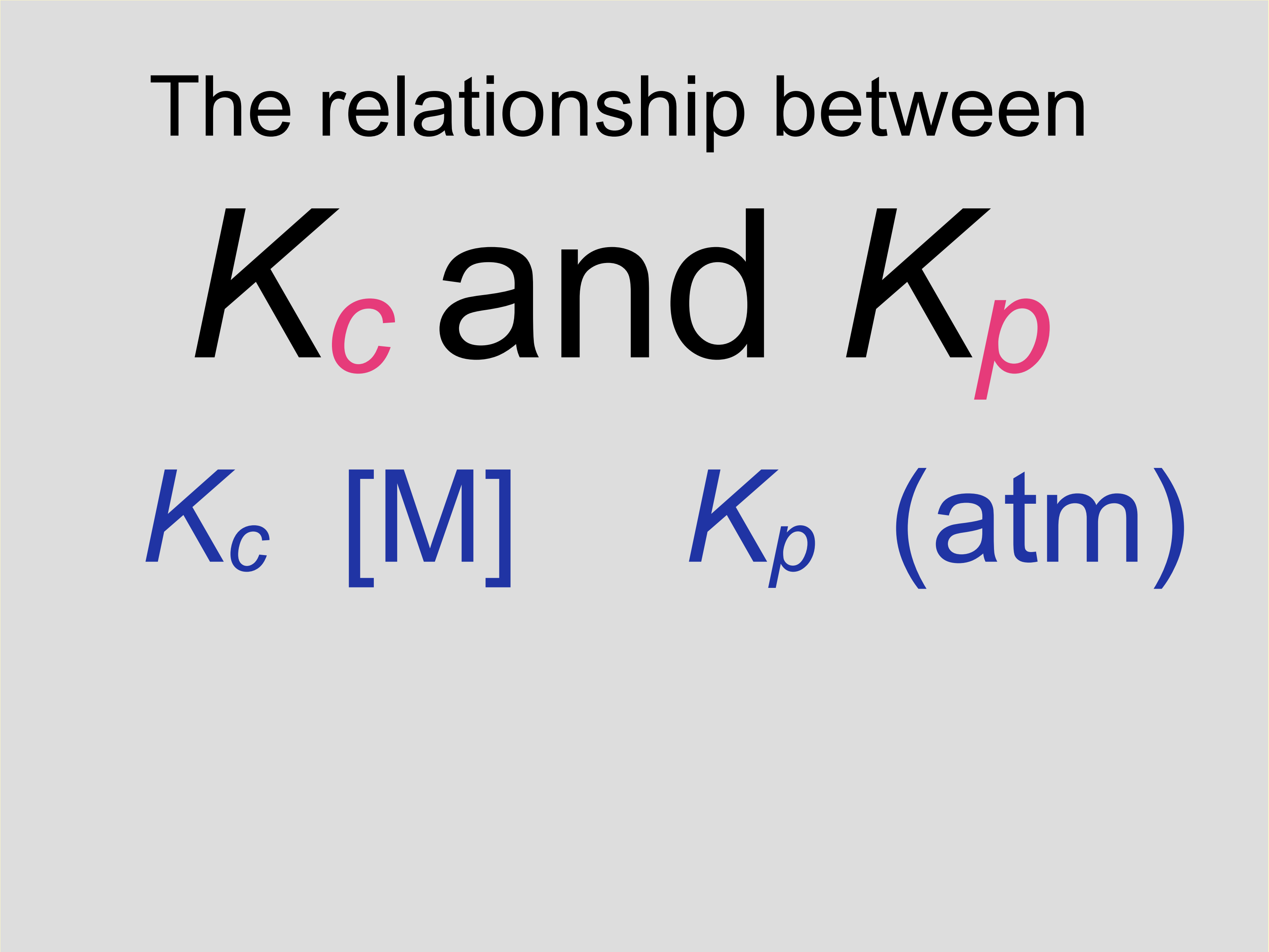
1. did not do any chemistry.
2. took a look at the text book.
3. did the sample problems in the text.
4. worked on the MC *or* FR
5. worked on the MC *and* FR
6. nearly finished *either* the MC *or* FR
7. nearly finished *both* MC *and* FR

LAD F.1 $Fe^{3+} + SCN^{-} \rightleftarrows [FeSCN]^{2+}$



- 10 Test Solutions 1-5.5
  - ✓ Assumed $[SCN^{-}]_o = [FeSCN]^{2+}_{eq}$
  - ✓ measured Abs, constructed graph
- took a look at the text book.
- did the sample problems in the text.
- worked on the MC *or* FR
- worked on the MC *and* FR
- nearly finished *either* the MC *or* FR
- nearly finished *both* MC *and* FR

No Longer Part of the AP Curriculum



The relationship between

K_c and K_p

K_c [M] K_p (atm)

Relationship of K_c to K_p

- Since PV = nRT
  - $P = \left(\dfrac{n}{V}\right)RT \qquad \left(\dfrac{n}{V}\right) = \dfrac{P}{RT} \qquad \left(\dfrac{n}{V}\right) = molarity$
  - We can substitute $\dfrac{P}{RT}$ into the K_c equation
  - For $A_{(g)} + 3B_{(g)} \leftrightarrows 2C_{(g)}$

$$K_c = \frac{[C]^2}{[A][B]^3} \qquad K_c = \frac{\left[\dfrac{P}{RT}\right]^2}{\left[\dfrac{P}{RT}\right]\left[\dfrac{P}{RT}\right]^3}$$

For $A_{(g)} + 3B_{(g)} \leftrightarrows 2C_{(g)}$

$$K_c = \frac{\left[\frac{P}{RT}\right]^2}{\left[\frac{P}{RT}\right]\left[\frac{P}{RT}\right]^3}$$

Factor out the RT’s

$$K_c = \frac{\left(P_c\right)^2}{\left(P_A\right)\left(P_B\right)^3}\frac{\left(\frac{1}{RT}\right)^2}{\left(\frac{1}{RT}\right)\left(\frac{1}{RT}\right)^3}$$

The first factor above is K_p
Clean up the RT factors

$$K_c = K_p\frac{1}{\left(\frac{1}{RT}\right)^2}$$

Use a little
more Algebra

$$K_c = K_p\left(RT\right)^2$$

For $A_{(g)} + 3B_{(g)} \leftrightarrows 2C_{(g)}$

- So $K_c = K_p(RT)^2$ …and lets go back to the original reaction to notice that for
  - $A_{(g)} + 3B_{(g)} \leftrightarrows 2C_{(g)}$
    - ✳ $\sum_{\text{Reactant coefficients}} - \sum_{\text{Product coefficients}} = 2$
- *So here's the punch line:*
- $K_c = K_p(RT)^{\Delta n(\text{react-prod})}$
- $K_p = K_c(RT)^{\Delta n(\text{prod-react})}$
  - ~~(this one is on your blue sheet in the Equilibrium Section)~~

The relationship between

K_c and K_p

K_c [M] K_p (atm)

Relationship of K_c to K_p

- Since PV = nRT
  - $P = \left(\frac{n}{V}\right)RT$ $\left(\frac{n}{V}\right) = \frac{P}{RT}$ $\left(\frac{n}{V}\right) = molarity$
  - We can substitute $\frac{P}{RT}$ into the K_c equation
  - For $A_{(g)} + 3B_{(g)} \leftrightarrows 2C_{(g)}$

$$K_c = \frac{[C]^2}{[A][B]^3} \qquad K_c = \frac{\left[\frac{P}{RT}\right]^2}{\left[\frac{P}{RT}\right]\left[\frac{P}{RT}\right]^3}$$

For $A_{(g)} + 3B_{(g)} \leftrightarrows 2C_{(g)}$

$$K_c = \frac{\left[\dfrac{P}{RT}\right]^2}{\left[\dfrac{P}{RT}\right]\left[\dfrac{P}{RT}\right]^3}$$

Factor out the RT's

$$K_c = \frac{(P_c)^2}{(P_A)(P_B)^3}\,\frac{\left(\dfrac{1}{RT}\right)^2}{\left(\dfrac{1}{RT}\right)\left(\dfrac{1}{RT}\right)^3}$$

The first factor above is K_p

Clean up the RT factors

$$K_c = K_p \frac{1}{\left(\dfrac{1}{RT}\right)^2}$$

Use a little more Algebra

$$K_c = K_p (RT)^2$$

For $A_{(g)} + 3B_{(g)} \leftrightarrows 2C_{(g)}$

- So $K_c = K_p(RT)^2$ …and lets go back to the original reaction to notice that for
  - $A_{(g)} + 3B_{(g)} \leftrightarrows 2C_{(g)}$
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- *So here's the punch line:*
- $K_c = K_p(RT)^{\Delta n(\text{react-prod})}$
- $K_p = K_c(RT)^{\Delta n(\text{prod-react})}$
  - (this one used to be on your formula sheet in the Equilibrium Section)

$PCl_{5(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)} \quad \Delta H = +87.9\ kJ$

- For the reaction above, if $K_p = 10$ at 25ºC, calculate K_c at the same temperature.

1. 10
2. 0.41
3. 24
4. 240
5. there is no way to calculate K_c from K_p

$PCl_{5(g)} \leftrightarrows PCl_{3(g)} + Cl_{2(g)}$ $\Delta H = +87.9$ kJ

- For the reaction above, if $K_p = 10$ at 25ºC, calculate K_c at the same temperature.

- $K_c = K_p(RT)^{(1 \text{ reactant } - 2 \text{ products})}$

or $(K_p = K_c(RT)^{(2 \text{ products } -1 \text{ reactant })}$

$$K_c = 10(0.0821 \times 298)^{-1} \qquad 10 = K_c(0.0821 \times 298)^{1}$$

$$K_c = \frac{10}{(0.0821 \times 298)} = 0.41$$

What if I am given K_c and I need K_p?

- Consider the reaction: $H_{2(g)} + I_{2(g)} \leftrightharpoons 2\ HI_{(g)}$
- The K_c is 50.5 at 25ºC
- What is the value for K_p?

What if I am given K_c and I need K_p?

- Consider the reaction: $H_{2(g)} + I_{2(g)} \leftrightarrows 2\ HI_{(g)}$
- The K_c is 50.5.
- What is the value for K_p?
- The # moles of gas is the same in both sides so in $K_p = K_c(RT)^{(2\ \text{products}\ -\ 2\ \text{reactants})}$
- $K_p = K_c(RT)^0$ and since $(RT)^0 = 1$
- In this case, $K_c = K_p$

$2\ NOCl_{(g)} \leftrightarrows 2NO_{(g)} + Cl_{2(g)}$

$K_c = 0.016$ at 945ºC

What is K_p at the same temp?

Select as many as apply.

You can use your calculator

1. 0.016
2. 0.625
3. 1.24
4. 1.6
5. 943
6. 1216
7. 162
8. 0.00016
9. Can not be determined with out concentration values.

$2\ NOCl_{(g)} \leftrightarrows 2NO_{(g)} + Cl_{2(g)}$

$K_c = 0.016$ at 945ºC

What is K_p at the same temp?

Select as many as apply.

1. 0.016
2. 0.625
3. 1.24
4. 1.6
5. 943
6. 1216
7. Can not be determined with out concentration values.

$$CO_{(g)} + 2\ H_{2(g)} \leftrightharpoons CH_3OH_{(g)}$$

$K_p = 3.6 \times 10^3$ at 450.°C

- Calculate K_c for the reaction at the same temperature.