Slide 1

Chemical Equilibrium

Chemistry in Two Directions

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Slide 2

Chemical Reactions

Up until now, we have talked about reactions as though they proceed in one direction: from left to right, as written in a balanced equation:

$$A_{(aq)} + 2\ B_{(aq)} \rightarrow 6\ C_{(aq)}$$

In fact, this is rarely true.

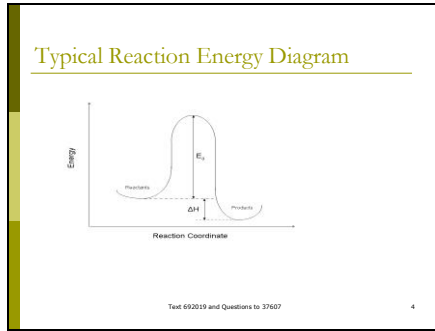Text 692019 and Questions to 37607   2

Slide 3

If you can go left, you can turn around and go right

If you consider the energetics of a reaction, it is usually represented by a graph of Energy vs. Reaction Coordinate

(Reaction Coordinate is complicated, but you can think of it as the lowest energy path between chemical species)

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Typical Reaction Energy Diagram

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Slide 5

What if you just flip it around?

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Slide 6

Everything is simply reversed:
The E_a is different, the ΔH is inverted

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Slide 7

Reactions can go both ways

- The hill is just higher going one way than the other.
- If it is exothermic going one way, it is endothermic going the other way.
- The world is reversible! (Well, except for time ☺)

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Slide 8

Implications for Chemical Reactions

The reversibility of chemical reactions means that rather than proceed from reactants to products, most reactions reach a state where there is no further change.

THIS DOES NOT MEAN NOTHING IS HAPPENING!

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Slide 9

DYNAMIC EQUILIBRIUM

Chemical Equilibrium is a **Dynamic Equilibrium.**

It is not that there is no reaction occurring, it is that the forward reaction and the reverse reaction are occurring at equal rates.

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Slide 10

$$A_{(aq)} + 2\,B_{(aq)} \leftrightarrow 6\,C_{(aq)}$$

6 C $_{(aq)}$ → A$_{(aq)}$ + 2 B$_{(aq)}$
Rate= $\frac{-\Delta[C]}{\Delta t}$ (C is disappearing)
AND
A$_{(aq)}$ + 2 B$_{(aq)}$ → 6 C $_{(aq)}$

Rate= $\frac{+\Delta[C]}{\Delta t}$ (C is being created)

Both reactions occur simultaneously with the Rate of destruction = rate of creation

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Slide 11

Stand ↔ Sit

This is a reaction…er, sort of.

Let's assume it is 1st order in both directions – doesn't matter, just makes it easy.

What is the rate law for the forward reaction?

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Slide 12

Stand ↔ Sit

Let's assume it is 1st order in both directions – doesn't matter, just makes it easy.

What is the rate law for the forward reaction?
A. Rate = k[Stand]
B. Rate = k[Sit]
C. ln[Stand]$_t$ =-kt+ln[Stand]$_0$
D. A and C
E. I can't tell without more information.

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Slide 13

Stand ↔ Sit

Let's assume it is 1st order in both directions – doesn't matter, just makes it easy.

What is the rate law for the Reverse reaction?

A. Rate = k[Stand]
B. Rate = k[Sit]
C. $\ln[Stand]_t = -kt + \ln[Stand]_0$
D. A and C
E. I can't tell without more information.

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Let's do the reaction!!!

Forward: Rate = ½ [Stand]
Reverse: Rate = ¼ [Sit]

There's 160 of you – all sitting.

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Time	Stand	Sit
0	0	160
	=1/2 [Stand]	=1/4[Sit]
	0-0+40=40	160-40+0=120
1	40	120
	½[Stand]=20	¼[Sit]=30
	40-20+30=50	120-30+20=110
2	50	110
	½[50]=25	¼[110]=27.5
	50+28-25=53	110-28+25 = 107
3	53	107
	½[53]=27	¼[107]=27

Slide 16

Equilibrium is Balance

- The forward and reverse reactions are balanced
- The concentrations of all species (reactants and products) become stable
- The equilibrium position is not the same for all reactions

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Slide 17

The Equilibrium Constant

The balance between forward and reverse reaction is summed up in the Equilibrium Constant ("K_{eq}")

$$K = \frac{[products]}{[reactants]}$$

If K is large, most of the reactants form products.

If K is small, most of the reactants stay as reactants

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Writing Equilibrium Constant Expressions

It is very simple to write the expression for "K_{eq}"

You simply take the concentration (molarity) of all gases, and solutions and raise them to their stoichiometric coefficient

You ignore pure liquids and solids – they don't have a "concentration" and their concentration is considered constant (a unitless 1) and so it doesn't contribute

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Slide 19

$A_{(aq)} + 2 B_{(aq)} \leftrightarrow 6 C_{(aq)}$

$$K_{eq} = \frac{[C]^6}{[B]^2[A]} = some\ number$$

Slide 20

$2 H_{2\ (g)} + O_{2\ (g)} \leftrightarrow 2 H_2O_{\ (g)}$

$$K_{eq} = \frac{[H_2O]^2}{[H_2]^2[O_2]}$$

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$2 H_{2\ (g)} + O_{2\ (g)} \leftrightarrow 2 H_2O_{\ (l)}$

$$K_{eq} = \frac{1}{[H_2]^2[O_2]}$$

Notice that the pure liquid is not included –
it doesn't really have a concentration and
so it becomes "1"

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$$2\ Na_{(s)} + Cl_{2\ (g)} \leftrightarrow 2\ NaCl_{\ (s)}$$

$$K_{eq} = \frac{1}{[Cl_2]}$$

Notice how the 2 solids do not contribute to the equilibrium constant

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$$H_2S_{\ (g)} + 2\ O_{2\ (g)} \leftrightarrow H_2SO_{4\ (g)}$$

$$K_{eq} = \frac{[H_2SO_4]}{[O_2]^2[H_2S]}$$

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Write the equilibrium constant expression:

$2\ HCl(aq) + CaCO_3(s) \rightarrow CaCl_2(aq) + H_2CO_3(aq)$

A. $K = \dfrac{[H_2CO_3][CaCl_2]}{[HCl]^2[CaCO_3]}$

B. $K = \dfrac{[H_2CO_3][CaCl_2]}{[HCl][CaCO_3]}$

C. $K = \dfrac{[H_2CO_3][CaCl_2]}{[HCl]^2}$

D. $K = \dfrac{[HCl]^2[CaCO_3]}{[CaCl_2][H_2CO_3]}$

E. $K = \dfrac{[HCl]^2}{[CaCl_2][H_2CO_3]}$

Slide 25

Different kinds of "K"

No matter what the subscript, K IS K IS K IS K IS K! They are all just equilibrium constants and they all get written and used the same way.

K_c K_p K_a K_b K_{sp} K_f K_w

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Slide 26

K_c vs K_p

□ When a reaction occurs in the gas phase, you can use the **partial pressure** of the gas instead of the concentration.

□ To separate the 2 different expressions, they are written differently:
  K_c = equilibrium constant with concentrations of species
  K_p = equilibrium constant with partial pressures of the species

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Slide 27

What is the preferred unit of concentration for a gas?

A M
B kg
C atm
D L
E Christian brothers

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Slide 28

Why is n/V of a gas only "sort of M"?

A. Christian brothers
B. Sisters of St. Joseph
C. V is not in L
D. V is not the solvent
E. V is a horrible TV show
F. V is victory – Sorry Team Canada
G. Church of Scientology-sorry Tom Cruise
H. Church of Heidi Klum – Sorry, sorry Seal
I. Your mother – sorry to your mother

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"Thermodynamic" K

$$K_{eq} = \frac{P_{O2}}{[H_2]}$$

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2Na(aq) + Cl$_2$ (g) = 2 NaCl (aq)

$$K_c = \frac{[NaCl]^2}{[Na]^2[Cl_2]}$$

$$K_{eq} = \frac{[NaCl]^2}{P_{Cl_2}[Na]^2}$$

No Kp

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If everything is a gas, you can use K_p

$H_2(g) + Cl_2(g) \leftrightarrow 2\ HCl(g)$

$K_c = \dfrac{[HCl]^2}{[H_2][Cl_2]}$

$K_p = \dfrac{P^2_{HCl}}{P_{H2}P_{Cl2}} = K_{eq}$

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Slide 32

K IS K IS K IS K IS K IS K

The subscripts – and we will see more of them – just tell you what specific type of reaction you are talking about.

Everything else about them is the same.

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Slide 33

Equilibrium Problems

- There are two main types of problems:
  - You know the concentrations and you are calculating the equilibrium constant
  - You know the equilibrium constant and you are calculating the concentrations
- Of course, there are nuances to these problems.

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Calculating the Equilibrium Constant

The only "trick" to calculating an equilibrium constant is that you must know the concentrations AT EQUILIBRIUM.

You cannot simply take any old concentrations at any old time. The reaction must have reached equilibrium

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Slide 35

A simple example

Hydrogen and oxygen gas will react to form steam (gaseous water). Hydrogen and oxygen gases were mixed in a 2 L flask at 450 C. After equilibrium was established, it was determined that there were 3 moles of water, 1.2 moles of hydrogen and 0.8 moles of oxygen in the flask. What is the equilibrium constant for this reaction at 450 C?

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Slide 36

A simple solution

1st you need a balanced equation:
$$2\ H_2\ _{(g)} + O_2\ _{(g)} \leftrightarrow 2\ H_2O\ _{(g)}$$

This allows us to immediately write the equilibrium constant expression:

$$K_c = \frac{[H_2O]^2}{[H_2]^2[O_2]}$$

□ $K_P = \frac{P^2_{H_2O}}{PH2^2PO2}$

All we need to know are the concentrations! But the must be the EQUILIBRIUM concentrations.

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Slide 37

A simple example

Hydrogen and oxygen gas will react to form steam (gaseous water). Hydrogen and oxygen gases were mixed in a 2 L flask at 450 C. **After equilibrium was established**, it was determined that there were 3 moles of water, 1.2 moles of hydrogen and 0.8 moles of oxygen in the flask. What is the equilibrium constant for this reaction at 450 C?

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Slide 38

A simple solution

Since we know the equilibrium concentrations:

$$\frac{1.2\ mol\ H_2}{2\ L} = 0.6\ M\ \ H_2$$

$$\frac{0.8\ mol\ O_2}{2\ L} = 0.4\ M\ \ O_2$$

$$\frac{3.0\ mol\ H_2O}{2\ L} = 1.5\ M\ \ H_2O$$

$$K_c = \frac{[H_2O]^2}{[H_2]^2[O_2]} = \frac{(1.5\ M)^2}{(0.6\ M)^2(0.4\ M)}$$

$K_c = 15.63$

Note: You could also calculate Kp by using the ideal gas law - more on that later.

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Slide 39

You canNOT use MOLES in K

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Slide 40

A Note about Units

Notice that I wrote the equilibrium constant without units even though the concentrations have units:

$$K_c = \frac{(1.5\ M)^2}{(0.6\ M)^2(0.4\ M)}$$

$K_c = 15.63$

Since the units of K will depend on stoichiometry, it doesn't have consistent units. It is always written as a UNITLESS QUANTITY!

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Slide 41

Clicker

H_2 and O_2 gas will react to form steam. H_2 and O_2 gases were mixed in a 3 L flask at 450 C. After equilibrium was established, it was determined that there were 1.5 moles of water, 2 moles of H_2 and 0.8 moles of O_2 in the flask. What is K_c at 450 C?

A. K=2.81   D. K=0.938
B. K=1.42   E. K=0.703
C. K=2.11

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A more complicated problem

Hydrogen and oxygen gas will react to form steam (gaseous water). 4.36 g of hydrogen and 28.6 g of oxygen were mixed in a 2 L flask at 250 C. After equilibrium was established, it was determined that there was 6.6 g of water What is the equilibrium constant for this reaction at 250 C?

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Slide 43

A series of simple calculations

1st you need a balanced equation:

$2 H_{2 (g)} + O_{2 (g)} \leftrightarrow 2 H_2O_{(g)}$

This allows us to immediately write the equilibrium constant expression:

$K_{eq} = K_c = \frac{[H_2O]^2}{[H_2]^2[O_2]}$

The question is: what are the equilibrium concentrations of all of the species?

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Determining the concentrations

ICE - ICE - BABY - ICE – ICE

The easiest way to solve this problem is by using an I-C-E chart ("ice chart") where I = initial concentration, C= change in concentration, and E = the equilibrium concentration.

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Slide 45

An ICE Chart

$2 H_{2 (g)} + O_{2 (g)} \leftrightarrow 2 H_2O_{(g)}$

Initial			
Change			
Equilibrium	I+C	I+C	I+C

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What do you know?

4.36 g hydrogen * $\dfrac{1\ mol\ H_2}{2.016\ g\ H_2}$ = 2.16 mol H_2

(this is the INITIAL amount)

28.6 g oxygen * $\dfrac{1\ mol\ O_2}{32.0\ g\ O_2}$ = 0.894 mol O_2

(this is the INITIAL amount)

6.6 g H_2O * $\dfrac{1\ mol\ H_2O}{18.02\ g\ H_2O}$ = 0.366 mol H_2O

(this is the EQUILIBRIUM AMOUNT)

Slide 47

UNITS! UNITS! UNITS!

An ICE chart can use EITHER moles or concentration (molarity) or even pressure (atm), but you must use only one of these in any single ICE chart.

K_c uses molarity, so it is usually easiest to use concentration

I will do the problem both ways!

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An ICE Chart

$2\ H_{2\ (g)} + O_{2\ (g)} \leftrightarrow 2\ H_2O_{\ (g)}$

Initial	2.16 mol	0.894 mol	0 mol
Change	?????	?????	??????
Equilibrium	????	?????	0.366 mol

What is the change in quantities?

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The "change" is all about stoichiometry!

$$2 H_{2\ (g)} + O_{2\ (g)} \leftrightarrow 2 H_2O_{\ (g)}$$

Initial	2.16 mol	0.894 mol	0 mol
Change	- 2 x	-x	+ 2 x
Equilibrium	????	?????	0.366 mol

Now it is easy to finish filling in the ICE chart!

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An ICE chart is really just "accounting for moles"

$$2 H_{2\ (g)} + O_{2\ (g)} \leftrightarrow 2 H_2O_{\ (g)}$$

Initial	2.16 mol	0.894 mol	0 mol
Change	- 2 x	-x	+ 2 x
Equilibrium	2.16 – 2 x=?	0.894 – x=?	2 x = 0.366 mol

It is often helpful to use an ICE chart for other types of problems, it is a great way to keep track of what is going on.

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Determining x allows me to fill in the rest of the chart

$$2 H_{2\ (g)} + O_{2\ (g)} \leftrightarrow 2 H_2O_{\ (g)}$$

Initial	2.16 mol	0.894 mol	0 mol
Change	- 2 x	-x	+ 2 x
Equilibrium	2.16 – 2 x	0.894 – x	2 x = 0.366 mol

2 x = 0.366 mol
x = 0.183 mol

Slide 52

Determining x allows me to fill in the rest of the chart

$$2 H_2 {}_{(g)} + O_2 {}_{(g)} \leftrightarrow 2 H_2O {}_{(g)}$$

	2.16 mol	0.894 mol	0 mol
Initial			
Change	- 2 (0.183 mol)	-0.183 mol	+ 2 (0.183 mol)
Equilibrium	2.16 – 2 (0.183) 1.794 mol	0.894 – 0.183 0.711 mol	0.366 mol

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Now we need to calculate the concentrations and put them into K_c

$$[H_2] = \frac{1.794\ mol}{2\ L} = 0.897\ M$$

$$[O_2] = \frac{0.711\ mol}{2\ L} = 0.356\ M$$

$$[H_2O] = \frac{0.366\ mol}{2\ L} = 0.183\ M$$

$$K_{eq} = K_c = \frac{[H_2O]^2}{[H_2]^2[O_2]}$$

$$K_c = \frac{[0.183\ M]^2}{[0.897\ M]^2[0.356\ M]}$$

$$K_c = 0.117$$

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We could do the same calculation using concentrations directly in the ICE chart

$$\frac{2.16\ mol\ H_2}{2\ L} = 1.08\ M$$

(this is the INITIAL concentration)

$$\frac{0.894\ mol\ O_2}{2\ L} = 0.447\ M$$

(this is the INITIAL concentration)

$$\frac{0.366\ mol\ H_2O}{2\ L} = 0.183\ M$$

(this is the EQUILIBRIUM concentration)

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An ICE Chart

$$2 H_{2\,(g)} + O_{2\,(g)} \leftrightarrow 2 H_2O_{(g)}$$

Initial	1.08 M	0.447 M	0 M
Change	- 2 x	-x	+ 2 x
Equilibrium	1.08 – 2x	0.447 - x	2x = 0.183 M

2x = 0.183 M
x = 0.0915 M

Slide 56

An ICE Chart

$$2 H_{2\,(g)} + O_{2\,(g)} \leftrightarrow 2 H_2O_{(g)}$$

Initial	1.08 M	0.497 M	0 M
Change	- 2 x	-x	+ 2 x
Equilibrium	1.08 – 2(0.0915) 0.897 M	0.447 – 0.0915 0.356 M	0.183 M

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Now we simply put the concentrations into K_c

$$K_{eq} = K_c = \frac{[H_2O]^2}{[H_2]^2[O_2]}$$

$$K_c = \frac{[0.183\,M]^2}{[0.897\,M]^2[0.356\,M]}$$

$$K_c = 0.117$$

Same answer as before!

Slide 58

How to use K_c

What if you already know the equilibrium constant? How do you use it?

If you know the equilibrium constant, you can use it to determine the equilibrium concentrations of all of the reacting species!

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Slide 59

An ICE Chart I+ C=E

$2 H_{2 (g)} + O_{2 (g)} \leftrightarrow 2 H_2O_{(g)}$

Initial			
Change	-2x	-x	+2x
Equilibrium	I+C	I+C	I+C

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Slide 60

Another Simple Problem

The K_c value for the formation of water from hydrogen and oxygen at 850 C is $4x10^{-6}$. If I mix 5.0 grams of hydrogen and 5.0 grams of oxygen in a 3 L flask at 850 C, what is the equilibrium concentration of the water?

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Slide 61

Another simple solution

1st you need a balanced equation:

$2 H_2 (g) + O_2 (g) \leftrightarrow 2 H_2O (g)$

This allows us to immediately write the equilibrium constant expression:

$$4 \times 10^{-6} = K_c = \frac{[H_2O]^2}{[H_2]^2[O_2]}$$

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Again, the Power of ICE

$2 H_2 (g) + O_2 (g) \leftrightarrow 2 H_2O (g)$

Initial			
Change	-2x	-x	+ 2 x
Equilibrium			

The "Change" line is always just stoichiometry

Slide 63

We already know a couple of things

5.0 g hydrogen * $\underline{1\ mol\ H_2}$ = 2.48 mol H_2
                    2.016 g H_2

$\underline{2.48\ mol\ H_2}$ = 0.827 M
3 L

5.0 g oxygen * $\underline{1\ mol\ O_2}$ = 0.156 mol O_2
                    32.0 g O_2

$\underline{0.156\ mol\ O_2}$ = 0.0533 M
 3 L

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Again, the Power of ICE

$2\ H_{2\ (g)} + O_{2\ (g)} \leftrightarrow 2\ H_2O_{(g)}$

Initial	0.827 M	0.0533 M	0 M
Change	-2x	-x	+ 2 x
Equilibrium	0.827 – 2 x	0.0533 – x	2 x

Now, we know everything – well, sort of.

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We have all of the equilibrium concentrations in terms of x…

…we can use K_c to solve for x

$$4 \times 10^{-6} = K_c = \frac{[H_2O]^2}{[H_2]^2[O_2]}$$

$$4 \times 10^{-6} = \frac{(2x)^2}{(0.827 - 2x)^2(0.0533 - x)}$$

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It looks like a mess…

…and it sort of is (although your calculator can probably solve it)

BUT you can simplify it with a helpful assumption:

ASSUME x<<0.0533

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If we assume x is small

$$4 \times 10^{-6} = K_c = \frac{[H_2O]^2}{[H_2]^2[O_2]}$$

$$4 \times 10^{-6} = \frac{(2x)^2}{(0.827 - 2x)^2(0.0533 - x)}$$

.0533-x ≈ 0.0533
0.827 − 2x ≈ 0.827

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I'm NOT assuming x=0

It's a question of scale.
I'm assuming x is so small that subtracting
(or adding) it doesn't change the value.

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I'm NOT assuming x=0

Bill Gates is worth $52.5 billion. If he gives
you $100, what is his net worth?

A. $52.5 billion
B. $52, 499,999,900
C. $52, 500,000,100
D. Who cares, it's a butt load of money,
   Brick.

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IT'S ALL ABOUT THE SIG FIGS, BENJAMIN!

$52,5_{00,000,000}$

- _____ 100

$52.5 billion to the right number of sig figs

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Slide 71

Don't forget to square EVERYTHING!

$$4 \times 10^{-6} = \frac{[2x]^2}{[0.827 - 2x]^2[0.0533 - x]}$$

$$4 \times 10^{-6} = \frac{[2x]^2}{[0.827]^2[0.0533]}$$

$$4 \times 10^{-6} = \frac{4x^2}{0.03645}$$

$$1.458 \times 10^{-7} = 4x^2$$

$$3.645 \times 10^{-8} = x^2$$

$$x = 1.91 \times 10^{-4}$$

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Slide 72

Is $x = 1.91 \times 10^{-4}$ really "much smaller than "0.0533"

A. Yes
B. No
C. Maybe, it depends
D. Yo, where'd you get the grenade, Brick?
E. Yo, momma

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Slide 73

Was the assumption good?

We started by assuming x<<0.0533

We now "know" that, with this assumption, x is 1.91×10^{-4}

Is $1.91 \times 10^{-4} << 0.0533$?

0.0533-0.000191=0.0531

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Critical Judgment

How small is small depends on how accurate an answer you need: If you need 1 sig fig, than any number that is a factor of 10-20 smaller is insignificant. If you need 2 sig figs, then it must be about 100 times smaller. If you need 3 sig figs it must be about 1000 times smaller.

A good general rule for our purposes is that if a number is <5% of another number, it is significantly smaller. This maintains 2 sig figs in all the concentrations – usually enough.

Slide 75

0.0533-x : x=1.91×10^{-4}

$$\frac{.0533}{20} = 0.00267$$

Compare 1.91×10^{-4} to 1/20th of 0.0533
IF $1.91 \times 10^{-4}<0.00267$, I call it "good assumption".
If $1.91 \times 10^{-4}>0.00267$, I call it "bad ass"

Slide 76

We put x back into the ICE chart

$$2\ H_{2\ (g)} + O_{2\ (g)} \leftrightarrow 2\ H_2O_{(g)}$$

Initial	0.827 M	0.0533 M	0 M
Change	$-2\ (1.91 \times 10^{-4})$	-1.91×10^{-4}	$+2\ (1.91 \times 10^{-4})$
Equilibrium	$0.827 - 2\ (1.91 \times 10^{-4})$ $= 0.827$	$0.0533 - 1.91 \times 10^{-4}$ $= 0.053_1$	3.8×10^{-4}

And we have our answer.

Slide 77

Clickers!

The K_c value for the formation of H_2O from H_2 and O_2 at 500 C is 3.2×10^{-4}. I put 5.0 mol of H_2 and 5.0 mol of O_2 in a 2 L flask at 500 C, what is the $[H_2O]$ at equilibrium?

A. 0.035 M   D. 0.070 M
B. 0.050 M   E. 0.100 M
C. 0.001 M

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First Exam

Yes, to graphing calculators – as long as there is no cheating.
Yes, to cell phone calculators – as long as there is no cheating.

You get 1 (ONE) 8-1/2 x 11 inch "formula sheet" – no restrictions.

Did I mention – NO CHEATING!

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Topics on 1st exam

1. Intermolecular forces – bp, mp, phase changes
2. Colligative properties – bp, mp, vp, osmotic pressure
3. Phase Diagrams
4. Heating/Cooling curves
5. Rate laws
6. Integrated Rate laws
7. Arrhenius Equation

Text 692019 and Questions to 37607   79

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Exam Review Homework

Online now.

Due at EIGHT 8 EIGHT 8 EIGHT p.m. Thursday.

Answer key will be available at 9 p.m on Thursday.

Text 692019 and Questions to 37607   80

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