Slide 1

Chemical Kinetics

How fast is it?

1

Slide 2

Reptiles

What happens to a lizard if it gets cold?

He hibernates.

Why?

2

Slide 3

The Blood is Cold…
…and so is the Chemistry

- Reptiles are cold-blooded. Their body temperature fluctuates with the external temperature.
- Cell functions are all chemical. If you change the conditions (temperature among them), the chemistry changes and they cannot function.

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Kinetics is all about SPEED

$$Rate = \frac{\Delta \, something}{\Delta time}$$

Rate of speed =

$$Rate = \frac{\Delta distance}{\Delta time} = \frac{miles \, traveled}{hour} \equiv \frac{km}{hour}$$

Reading speed =

$$Rate = \frac{words \, read}{time} = 250 \, words/minute$$

$$Walking \, dead = \frac{zombies \, killed}{second}$$

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Kinetics is all about the **rate** at which a reaction occurs. How fast are the reactants turned into products?

□ Consider a general reaction:

A + 2 B → 3 C
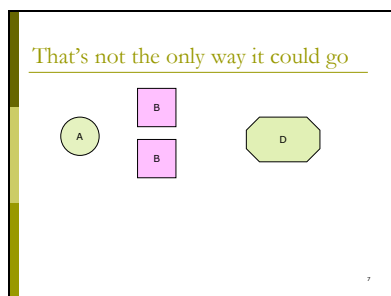
What happens in this reaction?

1 A and 2 B's make 3 C's

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How does it happen?

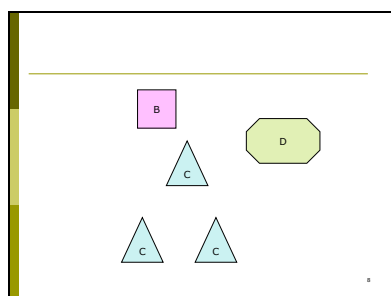

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That's not the only way it could go

A
B
B
D

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B
D
C
C
C

8

Slide 9

Regardless of how it actually happens…

The species all change in predictable (stoichiometric) fashion.

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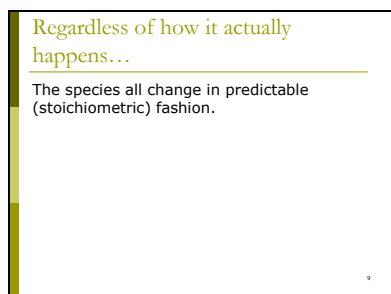
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A + 2 B → 3 C

Time	A	A reacts	B	B reacts	→	C	C produced
0 min	65		32			0	
		-1		-2			+3
1 min	64		30			3	
		-1		-2			+3
2 min	63		28			6	
		-10		-20			+30
60min	53		8			36	
		-4		-8			+12
90min	49		0			48	

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Kinetics is all about the **rate** at which a reaction occurs. How fast are the reactants turned into products?

- Consider a general reaction:
  A + 2 B → 3 C

There are a number of equivalent ways of looking at the rate of the reaction

---

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A + 2 B → 3 C

- If I want to measure the rate, I need to look at the **change** in something.

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$A + 2B \rightarrow 3C$

- If I want to measure the rate, I need to look at the **change** in something.
- I have 3 somethings:

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$A + 2B \rightarrow 3C$

- If I want to measure the rate, I need to look at the **change** in something.
- I have 3 somethings:
  - I could look at how fast A disappears.
  - I could look at how fast B disappears.
  - I could look at how fast C appears.

- All 3 representations of the rate should be equivalent!

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Rate

The **rate** of a reaction is how fast it is occurring. It is a measure of the **change in concentration** of the chemical species involved.

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Rate as a function of time

For my generic reaction:

$$A + 2\,B \rightarrow 3\,C$$

I have 3 different chemical species: A, B, and C.

I can measure the rate in terms of ANY OF THE 3 COMPOUNDS

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Rate as a function of time

$$A + 2\,B \rightarrow 3\,C$$

Rate is
Δ concentration/Δ time

Or

$\frac{\Delta[A]}{\Delta t}$ the change in [A] per unit time

$\frac{\Delta[B]}{\Delta t}$ the change in [B] per unit time

$\frac{\Delta[C]}{\Delta t}$ the change in [C] per unit time

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$A + 2\,B \rightarrow 3\,C$

Time	A	ΔA	Rate A	B	Δ B	Rate B	→	C	Δ C	Rate C
0 min	65			32				0		
		-1	$\frac{-1\,A}{1min}$		-2	$\frac{-2\,B}{1min}$			+3	$\frac{\pm 3\,C}{1min}$
1 min	64			30				3		
		-1	$\frac{-1\,A}{1min}$		-2	$\frac{-2\,B}{1min}$			+3	$\frac{\pm 3\,C}{1min}$
2 min	63			28				6		
		-10	$\frac{-10\,A}{58min}$		-20	$\frac{-20\,B}{58min}$			+30	$\frac{+30\,C}{58min}$
60min	53			8				36		

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Relationship between the different rates

A balanced equation has stoichiometry. This stoichiometry has meaning.

$$A + 2\,B \rightarrow 3\,C$$

If 1 mole of A reacted, 2 moles of B MUST have reacted also.

If 1 mole of A reacted, 3 moles of C MUST have been produced.

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Look at the different rates

Time	Rate A	Rate B	→	Rate C
0 min				
	-1 A / 1min	-2 B / 1min		+3 C / 1min
1 min				
	-1 A / 1min	-2 B / 1min		+3 C / 1min
2 min				
	-10 A / 58min	-20 B / 58min		+30 C / 58min
60min				

The rate at which B disappears is exactly twice the rate at which A disappears. The rate at which C appears is exactly 3 times the rate at which A disappears.

Why?

STOICHIOMETRY!!!

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The Algebra of rates

So, applying stoichiometry, for a given unit of time:

$\Delta[C] = -3\,\Delta[A],\ \Delta[B] = 2\,\Delta[A],\ 2\,\Delta[C] = -3\,\Delta[B]$

Or, in terms of the rates, themselves:

$2\,\dfrac{\Delta[A]}{\Delta t} = \dfrac{\Delta[B]}{\Delta t}\quad (\text{or, } \dfrac{\Delta[A]}{\Delta t} = \dfrac{1}{2}\dfrac{\Delta[B]}{\Delta t})$

$3\,\dfrac{\Delta[A]}{\Delta t} = -\dfrac{\Delta[C]}{\Delta t}\quad (\text{or, } \dfrac{\Delta[A]}{\Delta t} = -\dfrac{1}{3}\dfrac{\Delta[C]}{\Delta t})$

$3\,\dfrac{\Delta[B]}{\Delta t} = -2\,\dfrac{\Delta[C]}{\Delta t}\quad (\text{or, } \dfrac{\Delta[B]}{\Delta t} = -\dfrac{2}{3}\dfrac{\Delta[C]}{\Delta t})$

The negative sign is because C appears as A or B disappears.

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Practical Considerations

You can monitor the concentration of any species that is convenient to measure.

The rate is then calculated by taking the change in concentration divided by the change in time:

$$\frac{\text{final concentration} - \text{initial concentration}}{\text{final time} - \text{initial time}}$$

We then normalize it by dividing out the stoichiometry and..

...the rate is always a positive quantity, so take the absolute value of the number you get.

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FOUR different rates

1 A + 2 B = 3 C
We normalize for stoichiometry and take the absolute value.

Time	Rate A reacts	Rate of reaction	Rate B reacts	Rate of reaction	→	Rate C reacts	Rate of reaction
0 min							
	$\frac{-1\,A}{1\min}$	$\frac{1\,rxn}{1\,A}\frac{-1A}{1\,min} = \frac{1}{min}$	$\frac{-2\,B}{1\min}$	$\frac{1\,rxn}{2\,B}\frac{-2B}{1\,min} = \frac{1}{min}$		$\frac{+3\,C}{1\min}$	$\frac{1\,rxn}{3\,C}\frac{+3C}{1\,min} = \frac{1}{min}$

Only ONE rate of reaction
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A + 2 B → 3 C

Time	A	Rate A		B	Rate B		→	C	Rate C	
0 min	65			32				0		
		$\frac{-1\,A}{1\min}$	$\frac{1}{min}$		$\frac{-2\,B}{1\min}$	$\frac{1}{min}$			$\frac{+3\,C}{1\min}$	$\frac{1}{min}$
1 min	64			30				3		
		$\frac{-1\,A}{1\min}$	$\frac{1}{min}$		$\frac{-2\,B}{1\min}$	$\frac{1}{min}$			$\frac{+3\,C}{1\min}$	$\frac{1}{min}$
2 min	63			28				6		
		$\frac{-10\,A}{58\min}$	$\frac{10}{58min}$		$\frac{-20\,B}{58\min}$	$\frac{10}{58min}$			$\frac{+30\,C}{58\min}$	$\frac{10}{58min}$
60 min	53			8				36		

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THEY ARE THE SAME!

Time	Rate of reaction from A	Rate of reaction from B	→	Rate of reaction from C
0 min				
	$\frac{1}{\text{min}}$	$\frac{1}{\text{min}}$		$\frac{1}{\text{min}}$
1 min				
	$\frac{1}{\text{min}}$	$\frac{1}{\text{min}}$		$\frac{1}{\text{min}}$
2 min				
	$\frac{10}{58\text{min}}$	$\frac{10}{58\text{min}}$		$\frac{10}{58\text{min}}$
60min				

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Rate of reaction

ONE number for the reaction, no matter which molecule you were monitoring!

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Clicker Question

Suppose I make ammonia from the Haber Process:
$3 H_{2 (g)} + N_{2 (g)} \rightarrow 2 NH_{3 (g)}$

If I mix 3 moles of H_2 with an excess of N_2 and find that it takes 24 minutes for completion of the reaction, what is the rate of reaction?

A 0.125 mol/min
B 0.083 mol /min
C 0.042 mol /min
D 0.072 mol /min

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Rate

Rate = change in concentration
       change in time

Rate = Δconcentration
       Δtime

Rate = final concentration – initial concentration
       end time – initial time

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

3 moles of H_2 reacts in 24 minutes:

$$Rate\ of\ reaction\ of\ H_2 = \frac{0\ mol\ -\ 3\ mol}{24\ min}$$
$$= -0.125\ mol/min$$

$$Rate\ of\ H_2\ \mathbf{loss} = \frac{3\ mol\ lost}{24\ min} = 0.125\frac{mol}{min}$$

Rate of NH_3 production:
?

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

3 moles of H_2 reacts in 24 minutes:

Rate of NH_3 production:

$$3\ mol\ H_2 react\frac{2\ mol\ NH_3 made}{3\ mol\ H_2 react} = 2 mol\ NH_3\ made$$

$$Rate\ of\ NH_3\ production = \frac{2\ mol\ made}{24\ min} = 0.0833\frac{mol}{min}$$

$$Rate\ of\ N_2\ loss = \frac{1\ mol}{24\ min} = 0.0417\frac{mol}{min}$$

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

3 moles of H_2 reacts in 24 minutes:

$$Rate\ of\ H_2\ loss\ =\ 0.125\frac{mol}{min}$$

$$Rate\ of\ NH_3\ production\ =\ 0.0833\frac{mol}{min}$$

$$Rate\ of\ N_2\ loss\ =\ 0.0417\frac{mol}{min}$$

$$Rate\ of\ reaction\ =\ ???$$

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

Normalize for stoichiometry and take the absolute value:

$$Rate\ of\ reaction\ =\ \left|\frac{1}{3}rate\ of\ H_2 loss\right| = \left|\frac{1}{3}0.125\frac{mol}{min}\right|$$
$$=\ 0.0416\frac{mol}{min}$$

$$Rate\ of\ reaction\ =\ \left|\frac{1}{2}rate\ NH_3\ produced\right| = \left|\frac{1}{2}0.0833\frac{mol}{min}\right|$$
$$=\ 0.0416\frac{mol}{min}$$

$$Rate\ of\ reaction\ =\ \left|\frac{1}{1}rate\ of\ N_2 loss\right| = \left|\frac{1}{1}0.0416\frac{mol}{min}\right| =$$
$$0.0416\frac{mol}{min}$$

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$$Rate\ of\ reaction\ =\ 0.0416\frac{mol}{min}\ (unambiguously)$$

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Is the rate of a reaction constant?

□ Sometimes...but not usually.

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Is the rate of a reaction constant?

- ☐ Sometimes…but not always.
- ☐ Eventually, most reactions either:
  - ▪ Reach completion
  - ▪ Reach equilibrium (our NEXT topic!)

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Is the rate of a reaction constant?

- ☐ Sometimes…but not usually.
- ☐ Eventually, most reactions either:
  - ▪ Reach completion
  - ▪ Reach equilibrium
- ☐ When the concentrations stop changing, the "rate" is zero. So, the rate isn't usually constant forever, even if it is constant for a certain period of time.

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What does the rate depend upon?

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What does the rate depend upon?

- Why does a reaction stop?

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What does the rate depend upon?

- Why does a reaction stop?
  - you run out of a reactant (limiting reagent problem)
  - you reach equilibrium

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What does the rate depend upon?

- Why does a reaction stop?
  - you run out of a reactant (limiting reagent problem)
  - you reach equilibrium (equilibrium problem)
- In either case, it is the **concentration** that determines when it stops; you either reach equilibrium concentration, or you use up the total concentration of the limiting reagent.

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Rates MUST depend on concentration!

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It's all very logical…

After all, let's say I want to do the following reaction:

$$H_2(g) + O_2(g) \rightarrow H_2O_2(g)$$

There's a lot of ways that reaction could happen. But, what's the one thing that definitely MUST happen for the reaction to take place?

H_2 and O_2 must find each other – Happy Valentine's Day!

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If you want to make friends…

…it helps to have a lot of other people around!

[You aren't going to make any friends sitting in your room watching Netflix! Helpful hint from your Uncle Joe.]

Same for reactions: the more H_2 and O_2 that are around, the more likely it is that an H_2 and an O_2 will find each other. [Simplifying.]

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We really don't care about rates…

Since rates of reaction tend to depend on concentration, any rate I measure is VERY SPECIFIC…and TEMPORARY.

As a reaction proceeds, you are constantly turning reactants into products. The rate is constantly changing.

We use rates a LOT. But rate is a tool to get us to something more generic.

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The Rate Law

- Our previous discussion proves that the rate must depend on the concentration.
- The **Rate Law** is the expression of the dependence of rate on the concentration of the reactants.

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The Rate Law
A + 2 B → 3 C

We expect the Rate to depend on A or B or both A and B.

Rate α [A]^x or Rate α [B]^y or Rate α [A]^x [B]^y

The superscripts "x" and "y" are called the **orders of the reaction** and represent the fact that the rate does not have to depend linearly on the concentration. "x" and "y" are usually integers or half-integers.

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The Rate Law
A + 2 B → 3 C

For the sake of discussion, assume that the rate depends linearly on both [A] and [B]

Rate α [A] [B]

To make the proportionality into an equality, we need to introduce the proportionality constant, k, which is called the **rate constant**

Rate = k[A][B]^2

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DON'T BE CONFUSED!

There are 3 terms in kinetics that can easily be mixed up:

Rate
Rate law
Rate constant

They are 3 very different things

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DON'T BE CONFUSED!

Rate – the change in concentration as a function of time

Rate law – the relationship between the rate and the concentrations of the reactants

Rate constant- the proportionality constant in the rate law. This is constant for a reaction at a given temperature.

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Reading a rate law

Rate = k[A][B]

The rate law above should be read as:

"The rate of reaction is 1st order in A, 1st order in B, and 2nd order overall"

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What do the orders mean?

1. <u>Algebraic:</u> The order is a measure of how strongly the rate depends on concentration: The higher the order, the more rapidly the rate of the reaction decreases toward 0.
2. <u>Chemical:</u> The orders are also indicative of the mechanism for the reaction (more later)

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A little more kinetics grammar

Rate = k [B]^2

"The rate is 2nd order in B and 2nd order overall."

Rate = k [A][B]^2

"The rate is 1st order in A, 2nd order in B, and 3rd order overall"

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It's all about the LAW…the RATE law…

The "rate" of a reaction depends on the concentration of reactants.

Mix-up something slightly different, the "rate" will be different.

The "rate" of a reaction is constantly changing because the amount of reactants is constantly changing.

SOOOO…it's the RATE LAW we care about.

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The Rate Law

The rate law gives the dependence of the observed rate on concentration.

As a result, if I know the rate law, I know what "rate" I see no matter what I mix together.

And, as we'll see later, if I know the rate law, I also know exactly how the rate is changing with time.

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Initial rates

Since the rate is not constant at all times, I can't really talk about the "rate" of a reaction in general. As a result, it is more common to talk about the **initial rate** of a reaction – the rate at the very beginning of a reaction before the concentrations have changed enough to make a huge difference in the rate.

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$$Rate = k[A]^{some\ power}\ [B]^{some\ other\ power}$$

To determine the rate law, I need to know two things:

1. The order of the reaction with respect to each reactant.
2. The rate constant.

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Where do the orders of a reaction come from?

The orders are related to the actual microscopic picture of reaction dynamics.

$$A + 2\ B \rightarrow 3\ C$$

The balanced equation gives the overall ratio of reactants to products. It doesn't tell you exactly how the reaction occurs.

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$A + 2\ B \rightarrow 3\ C$

One way the reaction *could* occur is exactly as written: 2 molecules of B and 1 molecule of A collide with each other and 3 molecules of C result.

This is NOT THE ONLY WAY

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$A + 2B \rightarrow 3C$

Another way this reaction *could* occur is the following sequence of reaction events:
1. $A \rightarrow 2D$ (fast)
    1 molecule of A falls apart into 2 D
2. $D + B \rightarrow E$ (slow)
    1 molecule of D collides with a molecule of B to form E.
3. $E + E \rightarrow 3C$ (fast)
    2 molecules of E collide to form 3 molecules of C

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The rate limiting step

1. $A \rightarrow 2D$ (fast)
2. $D + B \rightarrow E$ (slow)
3. $E + E \rightarrow 3C$ (fast)

Since the 2nd step is slow, the entire rate may only depend on that step. If so, the overall rate will only depend on the [B] since no A is involved.

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The orders tell us something about the molecular dynamics

If I know the rate law, it tells me something about the overall reaction dynamics.

$A + 2B \rightarrow 3C$

IF Rate = k[B], then the above reaction has a rate limiting step(s) depending only on B.

If Rate = k[A][B], then the above reaction has a rate limiting step(s) depending on A and B.

If Rate = k[A][B]^2, then the reaction occurs in a single step as written, involving 2 molecules of B and 1 molecule of A colliding.

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Knowing the rate law informs us on the molecular reaction dynamics.

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How do we determine the rate law?

- If we know the molecular dynamics, we can simply write the rate law. (For example, if I know 2 B molecules collide in the rate limiting step, then Rate = $k[B]^2$)

Slide 63

How do we determine the rate law?

- If we know the molecular dynamics, we can simply write the rate law. (For example, if I know 2 B molecules collide in the rate limiting step, then Rate = $k[B]^2$)
- More commonly, the rate law is determined experimentally by measuring the initial rate for a series of reaction mixtures. A process known as the **Method of Initial Rates**

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Initial rates

The **initial rate** of a reaction = the rate from time = 0 to a very short time later.

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A typical rate law problem.

Consider the reaction:
$NH_4+ + NO_2^- \rightarrow N_2 + 2 H_2O$

I must run (or have data) from a series of experimental runs of this reaction. Because k depends on Temperature, they must all be run at the same Temp.

Expt #	Initial [NH_4+]	Initial [NO_2^-]	Initial Rate (M/s)	Temp (K)
1	0.100 M	0.0050 M	1.35×10^{-7}	298
2	0.100 M	0.010 M	2.70×10^{-7}	298
3	0.200 M	0.010 M	5.40×10^{-7}	298

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Step 1 – Writing the generic rate law

I can't write the actual rate law – I don't know enough – but I can write a generic rate law for the reaction:

Rate = k [NH_4^+]^x [NO_2^-]^y

(REMEMBER, I don't know k, x, or y at this point.)

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Step 2 – A ratio of rates eliminates the rate constant.

$$Rate = k\,[NH_4^+]^x\,[NO_2^-]^y$$

1 equation with 3 unknowns is not solvable, BUT I can get rid of k by looking at the ration of 2 different rates because **k is constant.**

Expt #	Initial [NH4+]	Initial [NO2-]	Initial Rate (M/s)	Temp (K)
1	0.100 M	0.0050 M	1.35×10^{-7}	298
2	0.100 M	0.010 M	2.70×10^{-7}	298
3	0.200 M	0.010 M	5.40×10^{-7}	298

If I compare the rate of experiment #1 to Experiment #2, I get a ratio without k involved

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Step 2 - continued

Expt #	Initial [NH4+]	Initial [NO2-]	Initial Rate (M/s)	Temp (K)
1	0.100 M	0.0050 M	1.35 x 10-7	298
2	0.100 M	0.010 M	2.70 x 10-7	298
3	0.200 M	0.010 M	5.40 x 10-7	298

I can write a rate law for any of these experiments. I would need to know a few things to make it work, but I know what the rate law should look like:

$$Rate_1 = k[NH_4^+]_1^{order1}[NO_2^-]_1^{order2}$$

$$Rate_2 = k[NH_4^+]_2^{order1}[NO_2^-]_2^{order2}$$

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Step 2 - continued

Expt #	Initial [NH4+]	Initial [NO2-]	Initial Rate (M/s)	Temp (K)
1	0.100 M	0.0050 M	1.35 x 10-7	298
2	0.100 M	0.010 M	2.70 x 10-7	298
3	0.200 M	0.010 M	5.40 x 10-7	298

$$Rate_1 = k[NH_4^+]_1^{order1}[NO_2^-]_1^{order2}$$

$$Rate_2 = k[NH_4^+]_2^{order1}[NO_2^-]_2^{order2}$$

I can compare these two rates. They are different, but they both obey the same rate law:

$$\frac{Rate_1}{Rate\,2} = \frac{k[NH_4^+]_1^x[NO_2^-]_1^y}{k[NH_4^+]_2^x[NO_2^-]_2^y} = \frac{[NH_4^+]_1^x[NO_2^-]_1^y}{[NH_4^+]_2^x[NO_2^-]_2^y}$$

Conveniently, the "k" cancels. One less thing I don't know!

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Step 2 - continued

Expt #	Initial [NH4+]	Initial [NO2-]	Initial Rate (M/s)	Temp (K)
1	0.100 M	0.0050 M	1.35 x 10-7	298
2	0.100 M	0.010 M	2.70 x 10-7	298
3	0.200 M	0.010 M	5.40 x 10-7	298

$$\frac{Rate_1}{Rate\ 2} = \frac{[NH_4^+]_1^x[NO_2^-]_1^y}{[NH_4^+]_2^x[NO_2^-]_2^y}$$

There are only 2 unknowns left, which is still too many, but look at the concentration data – Experiment 1 and Experiment 2 have the SAME concentration of NH_4^+ - this is not an accident!

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Step 3 – Use the identical concentrations to eliminate all but one of the orders

$$\frac{Rate_1}{Rate\ 2} = \frac{[NH_4^+]_1^x[NO_2^-]_1^y}{[NH_4^+]_2^x[NO_2^-]_2^y}$$

$$\frac{1.35 \times 10^{-7}}{2.70 \times 10^{-7}} = \frac{[0.100]_1^x[0.0050]_1^y}{[0.100]_2^x[0.010]_2^y}$$

This can also be written as:

$$\frac{1.35 \times 10^{-7}}{2.70 \times 10^{-7}} = \frac{[0.100]_1^x}{[0.100]_2^x} \cdot \frac{[0.0050]_1^y}{[0.010]_2^y}$$

No matter what x is, 0.100ˣ divided by 0.100ˣ is still 1 and they cancel.

$$\frac{1.35 \times 10^{-7}}{2.70 \times 10^{-7}} = \frac{[0.0050]_1^y}{[0.010]_2^y}$$

We now have 1 equation with 1 unknown, this we can solve!   71

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Step 4 – Solve for the remaining order.

□ Sometimes, you can solve just by inspection:

$$\frac{1.35 \times 10^{-7}}{2.70 \times 10^{-7}} = \frac{[0.0050]_1^y}{[0.010]_2^y}$$

Doing the math results in:

$$0.5 = (0.5)^y$$

Clearly, y must be 1

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Step 4 – Solve for the remaining order using logs.

Whenever you are trying to deal with an exponent, you can always solve using logs:

$$0.5 = (0.5)^y$$

If you take the log of both sides:

$$\log (0.5) = \log (0.5)^y$$

But the log $A^y = y \log A$, so:

$$\log (0.5)^y = y \log (0.5)$$

Which gives: $\log(0.5) = y \log(0.5)$

$$y = \frac{\log(0.5)}{\log(0.5)} = 1$$

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The new rate law

We can now rewrite the rate law with the one known order.

Rate = k $[NH_4^+]^x$ $[NO_2^-]^1$

To find x, we simply repeat the process using the other experimental data.

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Determining x

Expt #	Initial [NH₄+]	Initial [NO₂-]	Initial Rate (M/s)	Temp (K)
1	0.100 M	0.0050 M	1.35×10^{-7}	298
2	0.100 M	0.010 M	2.70×10^{-7}	298
3	0.200 M	0.010 M	5.40×10^{-7}	298

Notice that Experiments 2 and 3 have the same $[NO_2^-]$. This means that if we look at the ratio of $Rate_2/Rate_3$ that term (along with k) drops out and we only have x left.

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Solving for x

$$\frac{2.70 \times 10^{-7}}{5.40 \times 10^{-7}} = \frac{[0.100]_1^x \, [0.010]_1^y}{[0.200]_2^x \, [0.010]_2^y}$$

$$\frac{2.70 \times 10^{-7}}{5.40 \times 10^{-7}} = \frac{[0.100]_1^x}{[0.200]_2^x}$$

$$0.50 = 0.50^x$$

$$x = 1$$

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The final rate law

Rate = k $[NH_4^+]^1 \, [NO_2^-]^1$

The reaction is 1st order in ammonium, 1st order in nitrite, and 2nd order overall. All we need now is k!

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Determining the rate constant

The rate constant can easily be determined by using the experimental data. With x and y now know, k is the only unknown.

But we have 3 experiments, which one do we use?

ALL 3 OF THEM!

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Determining k by taking the average of the experiments

Ideally, k should be identical for all 3 experiments.

Since these are "real" experiments, they have real experimental errors. They might be slightly different for the 3 different mixtures. The best value for k is the average of all 3 trials.

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Expt #	Initial [NH_4^+]	Initial [NO_2^-]	Initial Rate (M/s)	Temp (K)
1	0.100 M	0.0050 M	1.35 x 10-7	298
2	0.100 M	0.010 M	2.70 x 10-7	298
3	0.200 M	0.010 M	5.40 x 10-7	298

$Rate = k [NH_4^+]^1 [NO_2^-]^1$

$Rate_1 = 1.35 \times 10^{-7} = k (0.100)(0.0050)$

$k_1 = 2.7 \times 10^{-4}$

$Rate_2 = 2.70 \times 10^{-7} = k (0.100)(0.010)$

$k_2 = 2.7 \times 10^{-4}$

$Rate_3 = 5.40 \times 10^{-7} = k (0.200)(0.010)$

$k_3 = 2.7 \times 10^{-4}$

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My "real" data isn't really "real"!

□ Obviously, this data is too perfect, but you get the idea.

□ $k_{avg} = 2.7 \times 10^{-4}$ and this is the number we use to complete the rate law:

$Rate = 2.7 \times 10^{-4} M^{-1}s^{-1} [NH_4^+]^1 [NO_2^-]^1$ at 298 K

(Remember, k is temp dependent)

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T-dependence of k

It shouldn't be a big surprise that the rate of a reaction is related to the energetics of the reaction.

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The hard part is getting over the hump.

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E_a = Activation Energy

The tale of a reaction is not limited strictly to the identity and energetics of the products and reactants, there is a path (reaction coordinate) that must get followed.
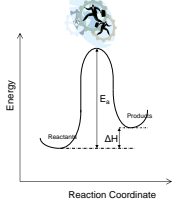
The "hump" represents a hurdle that must be overcome to go from reactants to products.

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How do you get over the hump?

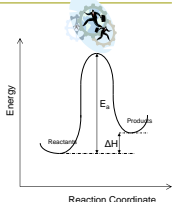If you are at the top, it is easy to fall down into the valley (on either side), but how do you get to the top?

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How do you get over the hump?

The molecules acquire or lose energy the same way: by colliding with each other!

The energy comes from the "bath", the rest of the system.

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T dependence of k

▫ The dependence of k on Temperature is given by the Arrhenius equation:

$$k = A\,e^{-Ea/RT}$$

where A is the Arrhenius constant (collision factor), E_a is the activation energy, R is the ideal gas constant, and T is the absolute temperature (Kelvin)

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How do we use the Arrhenius Equation?

There are 2 possible ways to use it:

1. Graphically
 If I take the ln of both sides, I get:
$$\ln k = -\frac{Ea}{R}\frac{1}{T} + \ln A$$
Notice, this looks like the equation of a straight line (y = mx+b) where y=ln k, $x = \frac{1}{T}$, $m = \frac{-Ea}{R}$ and b = ln A.

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Graphical use of the Arrhenius Equation

This is one way to determine the activation energy and collision (frequency) factor for a reaction: measure the rate constant at a number of different temperatures, plot ln k vs. 1/T and the slope gives you $-E_a/R$ and the intercept is ln A.

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If you don't want to make a graph

2. Mathematically

You can also use 2 data points (temperatures and rate
constants) and look at the relative rate constants:

$$\frac{k_1}{k_2} = \frac{A\ e^{-Ea/RT1}}{A\ e^{-Ea/RT2}}$$

Since Ea and A should both be constant for a reaction:

$$\frac{k_1}{k_2} = \frac{e^{-Ea/RT1}}{e^{-Ea/RT2}}$$

taking the log of both sides:

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{-Ea}{R}\left(\frac{1}{T1} - \frac{1}{T2}\right)$$

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Mathematical use of Arrhenius equation

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{-E_a}{R}\left(\frac{1}{T1} - \frac{1}{T2}\right)$$

Once I've used a pair of data points to
determine E_a, I can use the ln form of the
Arrhenius equation to determine k at any
temperature I want.

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Some practice problems

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N_2 (g) + Cl_2 (g) → 2 NCl (g)

The reaction was studied at -10° C.

$[N_2]_0$ (M)	$[Cl_2]_0$ (M)	Initial Rate (M/min)
0.10	0.10	0.18
0.10	0.20	0.71
0.20	0.20	1.45

What is the rate law?

A. Rate = $180M^{-2}s^{-1}$ $[N_2][Cl_2]^2$
B. Rate = $180M^{-1}s^{-1}$ $[N_2][Cl_2]$
C. Rate = $240 M^{-2}s^{-1}[N_2]^2[Cl_2]$
D. Rate = $180 M^{-2}s^{-1}[N_2]^2[Cl_2]$
E. Rate = $1800 M^{-3}s^{-1}[N_2]^2[Cl_2]^2$

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Problem #2 – I skipped #1

The reaction:

2 NO (g) + Cl_2 (g) → 2 NOCl (g)

was studied at -10° C. The following results were obtained for the rate of loss of Cl_2
(Rate = $-\Delta[Cl2]/\Delta t$)

$[NO]_0$ (M)	$[Cl_2]_0$ (M)	Initial Rate (M/min)
0.10	0.10	0.18
0.10	0.20	0.36
0.20	0.20	1.45

A. What is the rate law?
B. What is the rate constant?

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Problem #2 - solution

The general rate law can be written as:

Rate = $-\Delta[Cl2]/\Delta t$ = k $[NO]x[Cl2]y$

Comparing the initial rates of the first 2 reaction mixes:

$\dfrac{Rate\ 1}{Rate\ 2} = \dfrac{0.18}{0.36} = \dfrac{k\ [NO]_1{}^x[Cl_2]_1{}^y}{k[NO]_2{}^x\ [Cl_2]_2{}^y}$

$\dfrac{Rate\ 1}{Rate\ 2} = \dfrac{0.18}{0.36} = \dfrac{k\ (0.10)^x(0.10)^y}{k\ (0.10)^x(0.20)^y}$

$\dfrac{Rate\ 1}{Rate\ 2} = \dfrac{0.18}{0.36} = \dfrac{(0.10)^y}{(0.20)^y}$

$0.5 = 0.5^y$

ln (0.5) = ln $(0.5)^y$ = y ln(0.5)
y = 1

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Problem #2 – solution cont'd

Similarly, by comparing rate 2 to rate 3, we get:

$\dfrac{\text{Rate 2}}{\text{Rate 3}} = \dfrac{0.36}{1.45} = \dfrac{k\,(0.10)^y(0.20)^x}{k(0.20)^y(0.20)^x}$

$\dfrac{0.36}{1.45} = \dfrac{(0.10)^y}{(0.20)^y}$

$0.248 = (0.5)^y$

$\ln(0.248) = y\,\ln(0.5)$

$y = \ln(0.248)/\ln(0.5) = 2.01$ approximately 2

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Problem #2 – solution cont'd

The rate law can then be written as:

Rate= k $[NO]^2[Cl_2]$

To determine the value of the rate constant, simply plug in the data from the chart and calculate k

0.18 M/min = k $(0.10\ M)^2(0.10\ M)$
k = 180 $M^{-2}\ min^{-1}$

These come out almost exactly the same for all 3 data points. In the case of data with some experimental spread to the numbers, calculate the k values for each set of data and average them.

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Problem #3

The reaction:

2 $I^-_{(aq)}$ + $S_2O_8^{2-}_{(aq)}$ → 6 $I_{2\ (aq)}$ + 2 SO_4^{2-}(aq)

was studied at 25° C. The following results were obtained for the rate of disappearance of $S_2O_8^{2-}$

[I-]₀ (M)	[S₂O₈²⁻]₀ (M)	Initial rate (M/s)
0.080	0.040	12.5x10-6
0.040	0.040	6.25x10-6
0.080	0.020	6.25x10-6
0.032	0.040	5.00x10-6
0.060	0.030	7.00x10-6

Determine the rate law and calculate the rate constant.

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Problem #3 – solution

Comparing the first and second reaction mix gives:

Rate 1 = $k[I-]^x [S2O8^{2-}]^y$
Rate 2 $k[I-]^x [S_2O_8^{2-}]^y$

$\frac{12.5 \times 10^{-6}}{6.25 \times 10^{-6}} = \frac{(0.080)^x}{(0.040)^x}$

$2 = 2^x$
$x = 1$

Comparing the first and third reaction mixes gives:

Rate 1 = $k[I-]^x [S2O8^{2-}]^y$
Rate 3 $k[I-]^x [S_2O_8^{2-}]^y$

$\frac{12.5 \times 10^{-6}}{6.25 \times 10^{-6}} = \frac{(0.040)^y}{(0.020)^y}$

$2 = 2^y$
$y = 1$

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Problem #3 – solution cont'd

So, the rate law is:
    Rate = $k [I-] [S_2O_8^{2-}]$

To determine k, we calculate it for all of the reaction mixtures and take the average:

Rate 1 = $12.5 \times 10^{-6} = k [0.080][0.040]$
$k1 = 3.91 \times 10^{-3} M^{-1}s^{-1}$
Rate 2 = $6.25 \times 10^{-6} = k [0.040][0.040]$
$k2 = 3.91 \times 10^{-3} M^{-1}s^{-1}$
Rate 3 = $6.25 \times 10^{-6} = k [0.080][0.020]$
$k3 = 3.91 \times 10^{-3} M^{-1}s^{-1}$
Rate 4 = $5.00 \times 10^{-6} = k [0.032][0.040]$
$k4 = 3.91 \times 10^{-3} M^{-1}s^{-1}$
Rate 5 = $7.00 \times 10^{-6} = k [0.060][0.030]$
$k5 = 3.89 \times 10^{-3} M^{-1}s^{-1}$

Average - $3.91 \times 10^{-3} {}^{-1} s$

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Tro 13.57

The activation energy of a reaction is 56.8 kJ/mol and the frequency factor is 1.5×10^{11} s^{-1}. Calculate the rate constant of the reaction at 25C.

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The activation energy of a reaction is 56.8 kJ/mol and the frequency factor is 1.5x10^{11} s^{-1}. Calculate the rate constant of the reaction at 25C.

$$k = Ae^{\frac{-E_a}{RT}}$$

$$k = 1.5 \times 10^{11}s^{-1}e^{\frac{-56.8\times10^3\frac{J}{mol}}{8.314\frac{J}{mol\,K}(25+273.15\,K)}}$$

$$k = 1.5 \times 10^{11}s^{-1}e^{-22.91414} = 16.8\ s^{-1}$$

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Tro 13.63

A reaction has a rate constant of 0.0117 /s at 400K and 0.689 /s at 450 K.

a. What is the value of the rate constant at 425 K?

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A reaction has a rate constant of 0.0117 /s at 400K and 0.689 /s at 450 K.

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{-E_a}{R}\left(\frac{1}{T1} - \frac{1}{T2}\right)$$

$$\ln\left(\frac{0.0117}{0.689}\right) = \frac{-E_a}{8.314\frac{J}{mol\,K}}\left(\frac{1}{400\,K} - \frac{1}{450\,K}\right)$$

$$-4.076 = \frac{-E}{8.314}(0.00250 - 0.002222)$$

E=121,996 J/mol

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a. What is the value of the rate constant at 425 K?

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{-E_a}{R}\left(\frac{1}{T1} - \frac{1}{T2}\right)$$

$$\ln\left(\frac{k}{0.689}\right) = \frac{-121996\,J/mol}{8.314\,\frac{J}{mol\,K}}\left(\frac{1}{425\,K} - \frac{1}{450\,K}\right)$$

$$\ln\left(\frac{k}{0.689}\right) = -1.9181$$

$$e^{\ln\left(\frac{k}{0.689}\right)} = e^{-1.9181}$$

$$\frac{k}{0.689} = 0.14688$$

k=0.101 s⁻¹

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Determine the rate law and k for the following reaction (in a 2.0 L flask) at 400 K:

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

P_{H2}	P_{O2}	Initial Rate	Temp
0.600 atm	0.300 atm	0.022 atm/s	500 K
0.300 atm	0.300 atm	0.012 atm/s	500 K
0.300 atm	0.600 atm	0.086 atm/s	500 K
0.300 atm	0.600 atm	0.103 atm/s	550 K

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What are the units of k?

A. s⁻¹
B. atm⁻¹s⁻¹
C. atm⁻²s⁻¹
D. atm⁻³s⁻¹
E. atm⁻⁴s⁻¹