Name: ______________________ Date: __________ Period: ______

HL Topic 6_ Kinetics - Guided Notes

Slide 3: Rate Law

- **Equation for a reaction that gives its rate as a function of reactant ____________.**
- Expresses the relationship of the rxn rate to a **rate constant (k)** and the ____________ of reactants.
- **X and y ARE NOT the same as the ____________ coefficients in a reaction.**
- $aA + bB \rightarrow cC + dD$
- Rate = $k[A]^x[B]^y$
- **x and y tell you the order of the ____________.**
- **x+y = overall ____________ order**

Slide 4: Example-Reaction Orders

- $2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$
- This reaction is experimentally determined to be second order with respect to NO and first order with respect to H_2
- The rate law would be written as:
- Rate = $k[NO]^2[H_2]$
- Overall reaction order: 2 + 1 = 3 (third-order reaction)

Slide 5: How To Determine Rate Laws

- Experimentally
- Found using ____________ rxn rates
- Reactant ____________ are varied and initial rates measured.
- Relationships between changing reactant ____________ and initial rates can then be deduced.

Slide 6: Determining Rate Laws Example

- Find two experiments where one reactant concentration changes and the other is held constant.
- Determine how the rates compare.
- Repeat for any additional reactants.
- If changing the reactant (A) concentration does not affect the rate, the reaction is zero-order with respect to A
- If changing the concentration of A produces a directly proportional change in rate, the reaction is first-order with respect to A.
- If changes in concentration of A lead to the square of that change in the rate of the reaction, the reaction is second-order with respect to A.
- $2H_2(g) + 2NO(g) \rightarrow 2H_2O(g) + N_2(g)$

Slide 7: Rate law:

Rate = k[NO]2[H2]

- Determining Rate Laws-Example
- 2+1 = 3, Reaction is third-order overall
- To solve for k, simply plug in data from any trial into the rate law.
- Trials 3 and 4: [NO] changes while [H_2] stays the same.
- 0.300/0.200 = 1.5
- $2.28 \times 10^{-5} / 1.01 \times 10^{-5} = 2.25$
- $(1.5)^2 = 2.25$, so **reaction is second-order with respect to NO**
- Trials 1 and 2: [H_2] changes while [NO] stays the same.
- Change in concentration: 0.200/0.100 = 2
- Change in rate: $5.05 \times 10^{-6}/2.53 \times 10^{-6} = 2$
- $(2)^1 = 2$, so **reaction is first-order with respect to H_2**

Slide 8: The Rate Constant (k)

- Determined ____________
- Unique for each ____________
- Changes depending on ____________

Slide 9: Reaction Orders: Zero-Order

- **Rate = $k[A]^0$**
- **Rate = k**
- **The ____________ of A does not affect the rate of the reaction.**

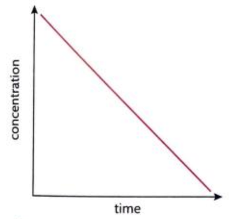


Figure 6.25 Concentration–time graph for a zero-order reaction.

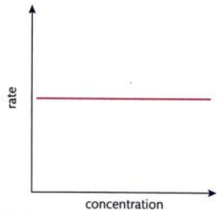


Figure 6.26 Rate–concentration graph for a zero-order reaction.

Slide 10: Reaction Orders: First-Order

- **Rate = *k*[A]**
- **The rate is directly proportional to the ____________ of A**

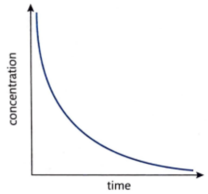


Figure 6.27 Concentration–time graph for a first-order reaction.

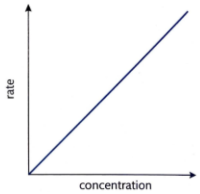


Figure 6.28 Rate–concentration graph for a first-order reaction.

Slide 11: Reaction Orders: Second-Order

- **Rate = *k*$[A]^2$**
- **The rate is proportional to the square of the ____________ of A**

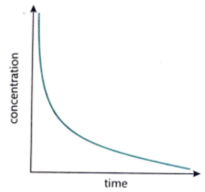


Figure 6.29 Concentration–time graph for a second-order reaction.

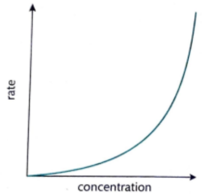
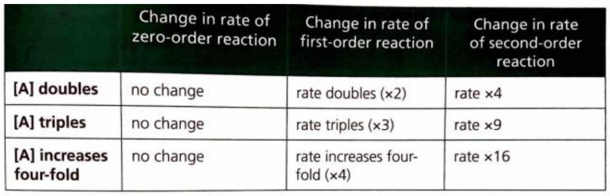
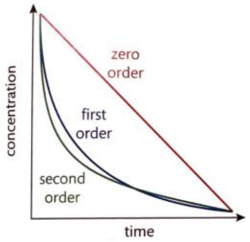


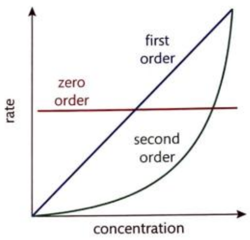
Figure 6.30 Rate–concentration graph for a second-order reaction.

Slide 12: Reaction Orders: Summary



	Change in rate of zero-order reaction	Change in rate of first-order reaction	Change in rate of second-order reaction
[A] doubles	no change	rate doubles (×2)	rate ×4
[A] triples	no change	rate triples (×3)	rate ×9
[A] increases four-fold	no change	rate increases four-fold (×4)	rate ×16





Slide 13: Turn and Talk

- The reaction of sodium thiosulfate (a clear liquid), with _____________ acid, results in an opaque solution. Design a simple experiment to determine the rate and reaction order of this reaction.
- $Na_2S_2O_3(aq) + 2HCl \rightarrow 2NaCl(aq) + SO_2(g) + S(s) + H_2O(l)$

Slide 14: Reaction Mechanism

- _____________ steps cannot be observed directly
- Reaction _____________ are *theories* regarding the sequence of events in a reaction.
- While reaction _____________ are based upon evidence, they cannot be absolutely **proven**.
- **The series of steps that make up a _____________ reaction.**
- ***Note: The _____________ steps in a reaction are called *elementary steps***

Slide 15: Intermediates

- The sum of the individual steps in a reaction mechanism must be equal to the overall reaction equation (_____________ cancel).
- **Products made in one step of a reaction that are used in a _____________ step.**

$$\begin{array}{rl} \text{step 1:} & NO_2(g) + \cancel{NO_2(g)} \rightarrow NO(g) + \cancel{NO_3(g)} \\ \text{step 2:} & \cancel{NO_3(g)} + CO(g) \rightarrow \cancel{NO_2(g)} + CO_2(g) \\ \hline \text{overall reaction:} & NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g) \end{array}$$

$$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$$

Slide 16: Molecularity

- _____________: an elementary step involves a single reactant particle.
- _____________**:** an elementary step involves two reactant particles.
- _____________**:** elementary steps involving three reactant particles (these are rare)
- **Indicates the number of reactant species involved in an _____________ step.**

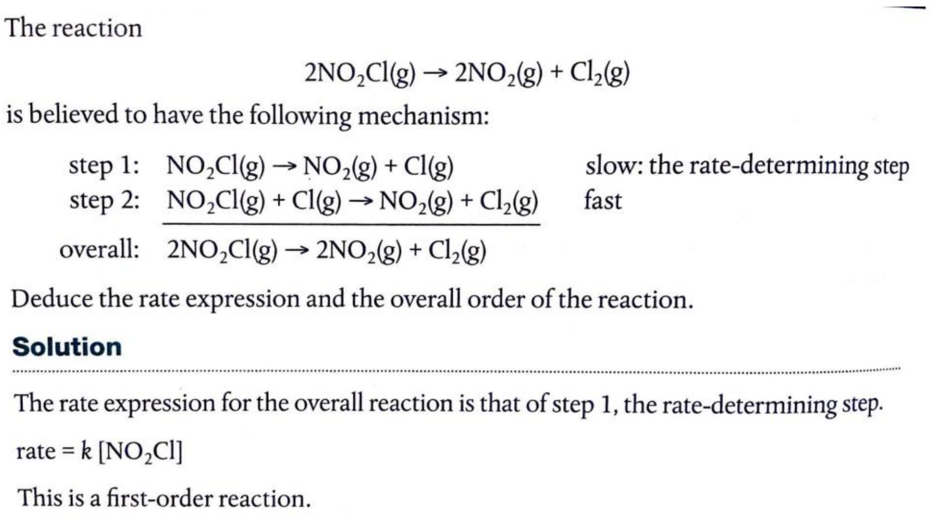
Slide 17: Rate-Determining Step

- **The slowest step in a _____________ sequence.**
- Products of a reaction can only appear as fast as the products of the rate-_____________ step.
- The rate-_____________ step determines the overall rate of the reaction.
- Activation energy for the overall reaction is equal to the activation energy of the rate-_____________ step.
- _____________ species present after the first step.

Slide 18: Rate Laws:Determined by the Reaction Mechanism

- Rate laws can be written for each step in a reaction ____________.
- The concentration of reactants in these ***elementary*** steps are included in the rate law **for that step**, raised to the power of the ____________ coefficient.
- The overall rate law comes from the **rate-____________ step** of the reaction.
- If a ____________ only consists of one step, then the rate law for that step is the same as the rate law for the overall reaction.

Slide 19: Example



The reaction

$$2NO_2Cl(g) \rightarrow 2NO_2(g) + Cl_2(g)$$

is believed to have the following mechanism:

step 1: $NO_2Cl(g) \rightarrow NO_2(g) + Cl(g)$ slow: the rate-determining step
step 2: $NO_2Cl(g) + Cl(g) \rightarrow NO_2(g) + Cl_2(g)$ fast
overall: $2NO_2Cl(g) \rightarrow 2NO_2(g) + Cl_2(g)$

Deduce the rate expression and the overall order of the reaction.

Solution

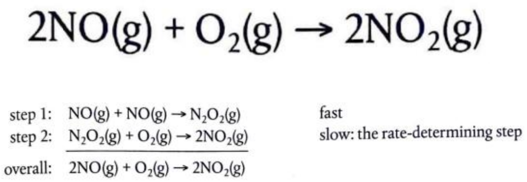
The rate expression for the overall reaction is that of step 1, the rate-determining step.

rate = $k\,[NO_2Cl]$

This is a first-order reaction.

Slide 20: You Try

- For the reaction:
- The following reaction mechanism has been proposed:
- What is the rate expression for the overall reaction and the reaction order?



$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

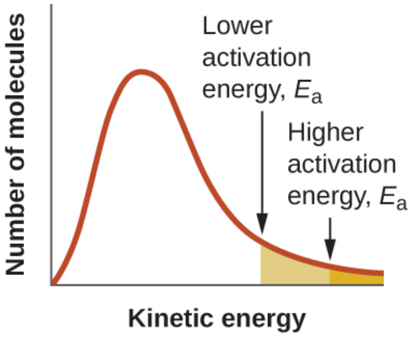
step 1: $NO(g) + NO(g) \rightarrow N_2O_2(g)$ fast
step 2: $N_2O_2(g) + O_2(g) \rightarrow 2NO_2(g)$ slow: the rate-determining step
overall: $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

Slide 21: Nuggets of Wisdom

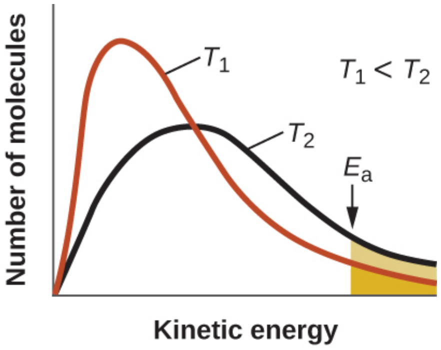
- The order of a reaction isn't dependent on the _____________ coefficients of the overall reaction, but it IS dependent on the stoichiometric coefficients of the rate-determining step.
- For a zero-order reaction, the reactant does not affect the overall rate, but that is because it is not involved in the rate-_____________ step.
- Remember, reaction mechanisms can not be proven, it can only be said they are consistent with _____________ data.

Slide 22: The Rate Constant is Dependent on Temperature

- Increasing the temperature does not change the _____________ of reactants.
- Since _____________ increases rate, according to the rate law, an increase in temperature affects the value of the rate constant, k.
- **If activation energy is low to begin with, increasing the _____________ does not have as large of an effect on the rate of reaction (if the activation energy is high, an increase in temperature would have a more significant effect on rate).**



(a)



(b)

Slide 23: Arrhenius Equation

- **A _____________ relationship that relates temperature, the rate constant, and activation energy.**
- **Can use the _____________ dependence of the rate constant to determine the activation energy.**
- **This _____________ is given is Section 1 of the data booklet.**

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

A – Arrhenius constant (frequency factor)

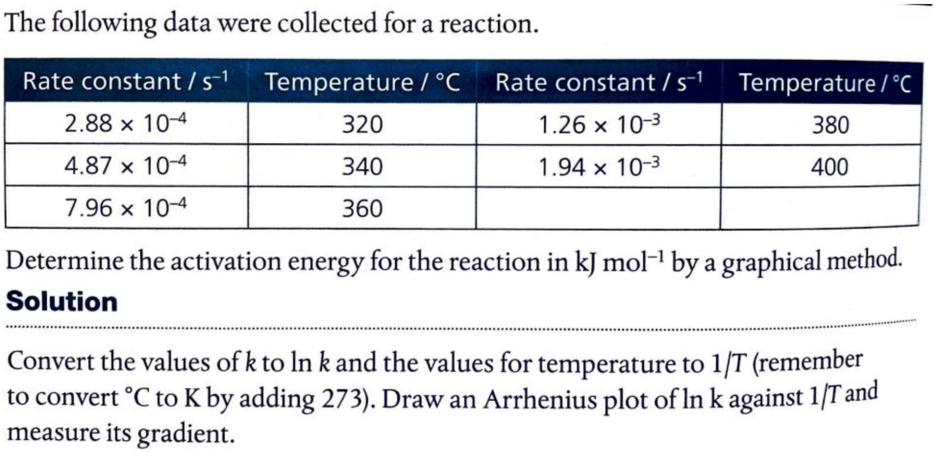
E_a – activation energy (J mol^{-1})

R – gas constant (8.31 J K^{-1} mol^{-1})

Slide 24: Arrhenius Plot

- Once the rate law is established, the rate constant can be determined for reactions at different ____________, and an Arrhenius plot can be made to determine the activation energy.
- Slope = -E_a/R
- **This graph is created by taking the natural log of both sides of the ____________ equation.**
- **E_a = slope (K) x 8.31 J K^{-1} mol^{-1}**

Slide 25: Example



The following data were collected for a reaction.

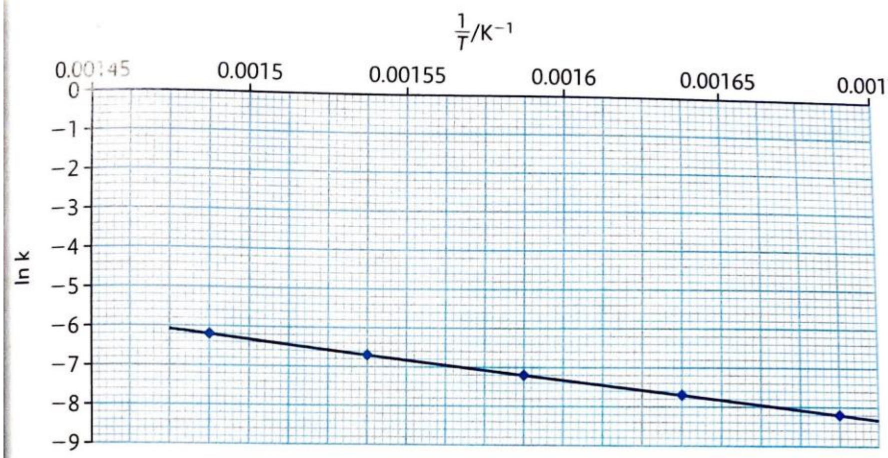
Rate constant / s^{-1}	Temperature / °C	Rate constant / s^{-1}	Temperature / °C
2.88×10^{-4}	320	1.26×10^{-3}	380
4.87×10^{-4}	340	1.94×10^{-3}	400
7.96×10^{-4}	360		

Determine the activation energy for the reaction in kJ mol^{-1} by a graphical method.

Solution

Convert the values of k to ln k and the values for temperature to $1/T$ (remember to convert °C to K by adding 273). Draw an Arrhenius plot of ln k against $1/T$ and measure its gradient.

Slide 26: Example Contd.



measured gradient = −9518.65 K

$$\text{gradient} = -\frac{E_a}{R}$$

E_a (J mol^{-1}) = 9518.65 (K) × 8.31 (J K^{-1} mol^{-1})

Therefore E_a = 79.1 kJ mol^{-1}

Slide 27: Another Way to Calculate Activation Energy

- The activation energy can be calculated by knowing the values of the rate constant at two ____________.
- The following equation can be derived by subtracting the natural log of the Arrhenius equation at two different ____________.

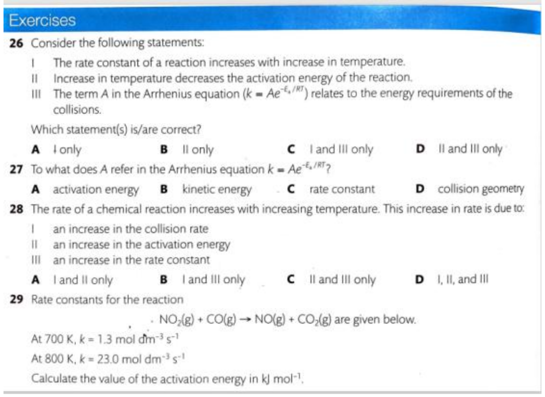
$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Slide 28: Example

Slide 29: Example Contd.

Slide 30: YOu Try!

- **Explain your reasoning.**



Exercises

26 Consider the following statements:

I The rate constant of a reaction increases with increase in temperature.
II Increase in temperature decreases the activation energy of the reaction.
III The term *A* in the Arrhenius equation ($k = Ae^{-E_a/RT}$) relates to the energy requirements of the collisions.

Which statement(s) is/are correct?

A I only **B** II only **C** I and III only **D** II and III only

27 To what does *A* refer in the Arrhenius equation $k = Ae^{-E_a/RT}$?

A activation energy **B** kinetic energy **C** rate constant **D** collision geometry

28 The rate of a chemical reaction increases with increasing temperature. This increase in rate is due to:

I an increase in the collision rate
II an increase in the activation energy
III an increase in the rate constant

A I and II only **B** I and III only **C** II and III only **D** I, II, and III

29 Rate constants for the reaction

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ are given below.

At 700 K, $k = 1.3\ mol\ dm^{-3}\ s^{-1}$
At 800 K, $k = 23.0\ mol\ dm^{-3}\ s^{-1}$
Calculate the value of the activation energy in $kJ\ mol^{-1}$.

Slide 31: Turn and Talk

- Considering collision theory, why do you think termolecular reactions are rare?

Slide 32: Turn and Talk

- How does a **steeper** slope in an Arrhenius plot relate to the activation energy of a reaction?