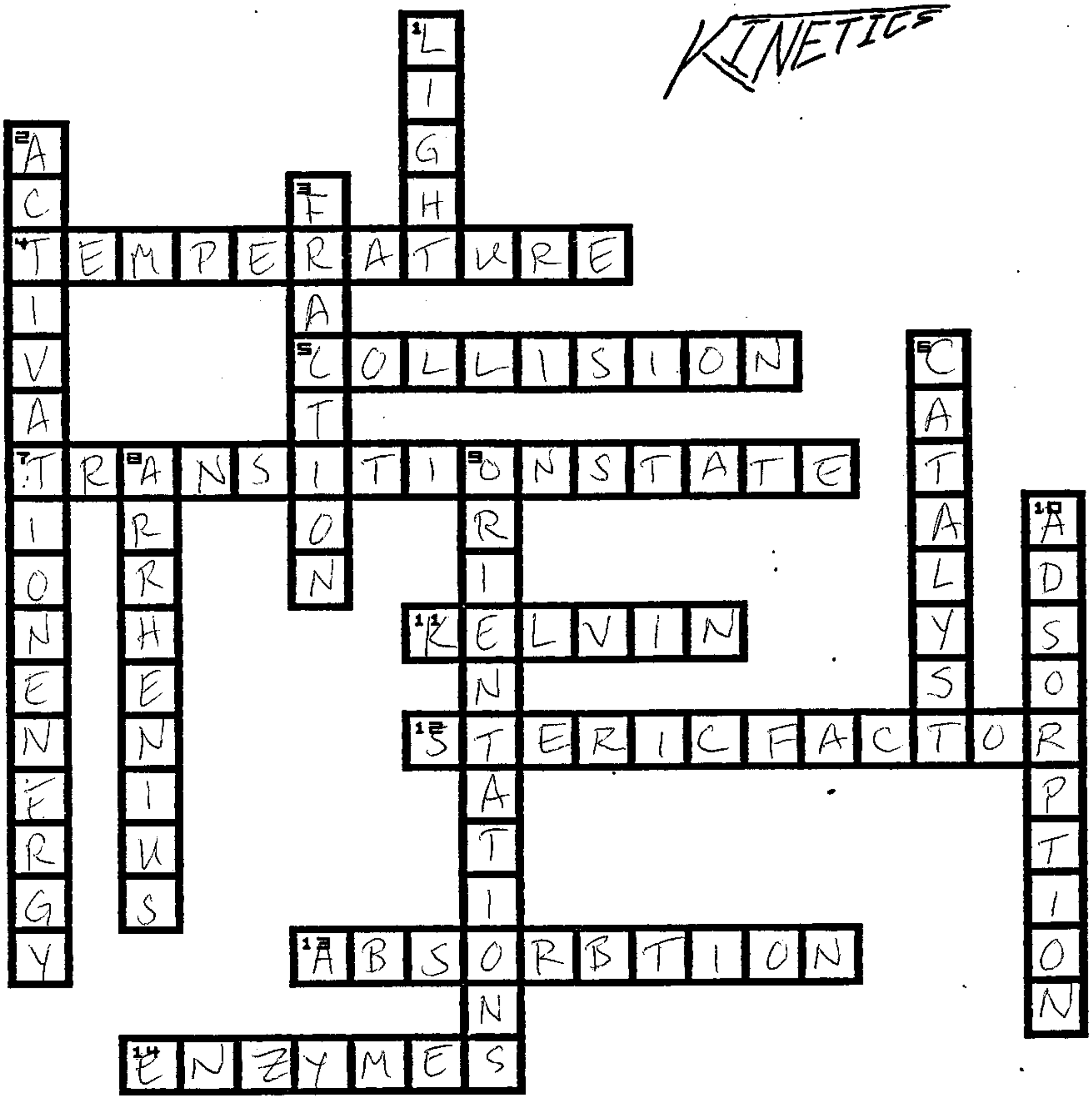
KINETICS



ACROSS CLUES

4. _______ affects reaction rate by varying the number of molecular collisions which occur.
5. The ______ model for chemical reactions can be used to explain observed behavior of rxn. rates.
7. The most unstable, or highest energy part of the reaction process is the ________.
11. In comparing reaction rate to temperature, we must use absolute temperature, or the _____ scale.
12. The ______ ______ is a fraction which represents how often molecules collide "reactably."
13. One substance penetrating into another is _______.
14. In humans, digestion is highly dependent on _______ to increase the rate of reaction.

DOWN CLUES

1. _____ is a form of radiation often used as a catalyst.
2. _____ _____ must be overcome for a reaction to occur.
3. Only a ______ of all molecular collisions will result in a reaction.
6. A substance used to speed up a chemical reaction is a(n) _______.
8. ______ simplified the rate constant equation for the collision model.
9. _______ of molecules toward each other determine whether or not molecules may react.
10. Collection of one substance on the surface of another is called ________.

Name: KEY

Date:

Chemistry II Practice Problems
Chapter 12 - Kinetics

1. The following data sets were collected for the reaction; A + B —> products

$[A]_o$ (mol/L)	$[B]_o$ (mol/L)	Initial Rates (mol/Ls)
0.10	0.20	0.030
0.20	0.20	0.059
0.20	0.30	0.060
0.30	0.30	0.090
0.30	0.50	0.090

x2, x1, x1, x1.5, x2, x1

∴ A is 1st order

∴ B is 0 order

Determine the form of the rate law, including the order of each reactant and the value of the rate constant. Also, write a pseudo–integrated rate law (in terms of one reactant) which would be applicable to this reaction

$Rate = k[A]^1[B]^0$ or $\boxed{Rate = k[A]}$

pseudo IRL: $\ln[A] = -kt + \ln[A]_0$

$k = \frac{Rate}{[A]} = 0.3\ s^{-1}$ (T1, 3, 4, 5)

$0.295\ s^{-1}$ (T2)

$0.299\ s^{-1}$ (Ave)

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2. The following data sets were collected for the reaction; NO + O_2 —> products

~~$[A]_o$~~ $[NO]_o$ (mol/L)	~~$[B]_o$~~ $[O_2]$ (mol/L)	Initial Rates (mol/Ls)
1×10^{18}	1×10^{18}	2.0×10^{16}
2×10^{18}	1×10^{18}	8.0×10^{16}
3×10^{18}	1×10^{18}	1.8×10^{17}
1×10^{18}	2×10^{18}	4.0×10^{16}
1×10^{18}	3×10^{18}	6.0×10^{16}

x2, x1, x4, x1, x2, x2

∴ NO is 2nd order

∴ $[O]_2$ is 1st order

Determine the form of the rate law, including the order of each reactant and the value of the rate constant.

$\boxed{Rate = k[NO]^2[O_2]}$

$k = \frac{Rate}{[NO]^2[O_2]} = 2 \times 10^{-38}$ (all trials)

$2 \times 10^{-38}\ L^2/mol^2\ s$

3

3. The following data sets were collected for the reaction;

$$2\,MnO_4^- + 5\,H_2C_2O_4 + 6\,H^+ \longrightarrow 2Mn^{2+} + 10\,CO_2 + 8\,H_2O$$

$[MnO_4^-]_o$ (mol/L)	$[H_2C_2O_4]_o$ (mol/L)	$[H^+]_o$ (mol/L)	Initial Rates (mol/Ls)
1×10^{-3}	1×10^{-3}	1.0	2.0×10^{-4}
x2 2×10^{-3}	same 1×10^{-3}	same 1.0	x4 8.0×10^{-4}
same 2×10^{-3}	x2 2×10^{-3}	same 1.0	x2 1.6×10^{-3}
same 2×10^{-3}	same 2×10^{-3}	x2 2.0	x1 1.6×10^{-3}

$\therefore MnO_4^-$ is 2nd order

$\therefore H_2C_2O_4$ is 1st order

$\therefore H^+$ is ZERO order

$$Rate = k[MnO_4^-]^2[H_2C_2O_4]$$

Determine the form of the rate law, including the order of each reactant and the value of the rate constant. **ALSO** — Write the $\boxed{\text{pseudo integrated rate law}}$ which could be used when $[H_2C_2O_4]_o$ is very much ~~larger~~ smaller than $\boxed{\text{the other concentrations.}}$

$\ln[H_2C_2O_4] = -kt + \ln[H_2C_2O_4]_o$

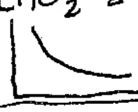
$$k = \frac{Rate}{[MnO_4^-]^2[H_2C_2O_4]} = 2 \times 10^5\ L^2/mol^2 \cdot s$$

(for each of the 4 trials)

4. Using the graphic method, determine the integrated rate law for the decay of $HO_2\bullet$ radicals according to the given data. Also determine the half-life of a sample of radicals which has an initial concentration of $\boxed{\text{one mole per cubic centimeter.}}$ $= 6.02 \times 10^{23}$ molec./cm3

$[HO_2\bullet]$ v. t

$\ln[HO_2\bullet]$ v. t



$1/[HO_2\bullet]$ v. t

2nd order

Time (s)	$[HO_2\bullet]$ (molecules/cm^3)
0	1.0×10^{11}
2	5.0×10^{10}
6	2.5×10^{10}
14	1.25×10^{10}
30	6.225×10^{9}

$$\boxed{\frac{1}{[HO_2\bullet]} = +kt + \frac{1}{[HO_2\bullet]_o}}$$

$$t_{1/2} = \frac{1}{k[HO_2\bullet]} = \frac{1}{(5.02 \times 10^{-12}\ cm^3/molec \cdot s)(6.02 \times 10^{23}\ molec/cm^3)}$$

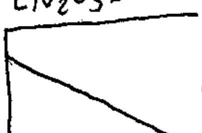
$k = slope = 5.02 \times 10^{-12}\ cm^3/molecule \cdot s$

$= 3.31 \times 10^{-13}\ s$

5. Given; $2\,N_2O_5 \longrightarrow 4\,NO_2 + O_2$ determine (a) the integrated rate law and rate constant, (b) the concentration of oxygen at 10 minutes, (c) the concentration of NO_2 at 40 minutes, and (d) the half-life for this reaction.

$[N_2O_5]$ v. t

$\ln[N_2O_5]$ v. t



1st order

$1/[N_2O_5]$ v. t

Time (min)	$[N_2O_5]$ (mol/L)
0	1.24×10^{-2}
10	0.92×10^{-2}
20	0.68×10^{-2}
30	0.50×10^{-2}
40	0.37×10^{-2}
50	0.28×10^{-2}
70	0.15×10^{-2}

(a) $\boxed{\ln[N_2O_5] = -kt + \ln[N_2O_5]_o}$

$k = -slope = -(-0.030098)$

$= 0.0301\ min^{-1}$

(b) $\Delta[N_2O_5] = 2 \times \Delta[O_2]$

$[O_2] = \frac{\Delta[N_2O_5]}{2} = \frac{(1.24 \times 10^{-2} - 0.92 \times 10^{-2})}{2}$

$= 1.6 \times 10^{-3}\ M$

(c) $[NO_2] = 2 \times \Delta[N_2O_5]$

$= 2 \times (1.24 \times 10^{-2} M - 0.37 \times 10^{-2} M)$

$= 0.0174\ M$

b & c are pure stoichiometry!! :)

Name: KEY

Support or refute the proposed mechanism.

Overall Reaction: $Cl_2 + CHCl_3 \rightarrow HCl + CCl_4$

Observed Rate Law: Rate = $k[Cl_2]^{1/2}[CHCl_3]$

$k_1[Cl_2] = k_{-1}[Cl]^2$ so $[Cl] = \sqrt{\frac{k_1}{k_{-1}}[Cl_2]}$

SUPPORT

$Cl_2 \leftrightarrow \cancel{2Cl}$ (Both fwd & rev are fast w/ equal rates)

$\cancel{Cl} + CHCl_3 \rightarrow HCl + \cancel{CCl_3}$ (Slow) Rate $= k_2[Cl][CHCl_3]$ ← substitute for the intermediate

Rate $= k_2\sqrt{\frac{k_1}{k_{-1}}}[Cl_2]^{\frac{1}{2}}[CHCl_3]$ meets Req. #2

$k_2\sqrt{\frac{k_1}{k_{-1}}} = k'$ so $\boxed{\text{Rate} = k'[Cl_2]^{\frac{1}{2}}[CHCl_3]}$

$\cancel{CCl_3} + \cancel{Cl} \rightarrow CCl_4$ (Fast)

$Cl_2 + CHCl_3 \rightarrow HCl + CCl_4$ ← meets requirement #1

Support or refute the proposed mechanisms.

Overall Reaction: $2\ NO + O_2 \rightarrow 2\ NO_2$

Observed Rate Law: Rate = $k[NO]^2[O_2]$

REFUTE

Proposed Mechanism A

$NO + O_2 \rightarrow NO_2 + \cancel{O}$ (Slow) Rate $= k_1[NO][O_2]$ Req. #2 $\boxtimes$ NO

$\cancel{O} + NO \rightarrow NO_2$ (Fast)

$2NO + O_2 \rightarrow 2NO_2$ Req#1 ☑ YES

SUPPORT

Proposed Mechanism B

$NO + O_2 \leftrightarrow \cancel{NO_3}$ (Both Fast with equal rates) $k_1[NO][O_2] = k_{-1}[NO_3]$ so $[NO_3] = \frac{k_1}{k_{-1}}[NO][O_2]$

$\cancel{NO_3} + NO \rightarrow 2NO_2$ (Slow) Rate $= k_2[NO_3][NO]$ ← substitute for the intermediate

Rate $= k_2\left(\frac{k_1}{k_{-1}}[NO][O_2]\right)[NO]$

Rate $= k'[NO]^2[O_2]$ Req. #2 ☑ YES!

$2NO + O_2 \rightarrow 2NO_2$ Req#1 ☑ YES!

REFUTE

Proposed Mechanism C

$2\ NO \rightarrow \cancel{N_2O_2}$ (Slow) Rate $= k_1[NO]^2$

$\cancel{N_2O_2} + O_2 \rightarrow \cancel{N_2O_4}$ (Fast) Req #2 $\boxtimes$ NO!

$\cancel{N_2O_4} \rightarrow 2NO_2$ (Fast) (oxygen is NOT zero order)

$2NO + O_2 \rightarrow 2NO_2$ Req#1 ☑ YES!

REFUTE

Proposed Mechanism D

$2\ NO \leftrightarrow \cancel{N_2O_2}$ (Both Fast with equal rates)

$\cancel{N_2O_2} \rightarrow NO_2 + \cancel{O}$ (Fast)

$\cancel{O} + NO \rightarrow NO_2$ (Fast)

$3NO \rightarrow 2NO_2$

NONSENSE requirement #1 $\boxtimes$ NO!

there's not even any oxygen anywhere in the mechanism!