



NATIONAL MATH + SCIENCE INITIATIVE

AP CHEMISTRY

Kinetics—Integrated

2016 EDITION

Click on the following link or scan the QR code
to complete the evaluation for the Study Session
https://www.surveymonkey.com/r/S_SSS



Periodic Table of the Elements

1 H 1.0079																	2 He 4.0026		
3 Li 6.941	4 Be 9.012															9 F 19.00	10 Ne 20.179		
11 Na 22.99	12 Mg 24.30	13 Al 26.98	14 Si 28.09	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948											35 Br 79.90	36 Kr 83.80
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.90	23 V 50.94	24 Cr 52.00	25 Mn 54.938	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80		
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 93.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29		
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)		
87 Fr (223)	88 Ra 226.02	89 †Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 S (269)	111 S (272)	112 S (277)	§Not yet named							

58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.4	63 Eu 151.97	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

*Lanthanide Series:

†Actinide Series:

AP Chemistry Equations & Constants

Throughout the test the following symbols have the definitions specified unless otherwise noted.

L, mL = liter(s), milliliter(s)

g = gram(s)

nm = nanometer(s)

atm = atmosphere(s)

mm Hg = millimeters of mercury

J, kJ = joule(s), kilojoule(s)

V = volt(s)

mol = mole(s)

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

E = energy

ν = frequency

λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34}$ J s

Speed of light, $c = 2.998 \times 10^8$ m s⁻¹

Avogadro's number = 6.022×10^{23} mol⁻¹

Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}, \text{ where } a A + b B \rightleftharpoons c C + d D$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

$$= K_a \times K_b$$

$$\text{pH} = -\log [H^+], \text{ pOH} = -\log [OH^-]$$

$$14 = \text{pH} + \text{pOH}$$

$$\text{pH} = \text{p}K_a + \log \frac{[A^-]}{[HA]}$$

$$\text{p}K_a = -\log K_a, \text{ p}K_b = -\log K_b$$

Equilibrium Constants

K_c (molar concentrations)

K_p (gas pressures)

K_a (weak acid)

K_b (weak base)

K_w (water)

KINETICS

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

k = rate constant

t = time

$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

$$P_A = P_{\text{total}} \times X_A, \text{ where } X_A = \frac{\text{moles A}}{\text{total moles}}$$

$$P_{\text{total}} = P_A + P_B + P_C + \dots$$

$$n = \frac{m}{M}$$

$$K = ^\circ\text{C} + 273$$

$$D = \frac{m}{V}$$

$$KE \text{ per molecule} = \frac{1}{2}mv^2$$

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure

V = volume

T = temperature

n = number of moles

m = mass

M = molar mass

D = density

KE = kinetic energy

v = velocity

A = absorbance

a = molar absorptivity

b = path length

c = concentration

Gas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

$$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$$

$$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$$

1 atm = 760 mm Hg

$$= 760 \text{ torr}$$

STP = 0.00°C and 1.000 atm

THERMOCHEMISTRY/ ELECTROCHEMISTRY

$$q = mc\Delta T$$

$$\Delta S^\circ = \sum S^\circ \text{ products} - \sum S^\circ \text{ reactants}$$

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$= -RT \ln K$$

$$= -nFE^\circ$$

$$I = \frac{q}{t}$$

q = heat

m = mass

c = specific heat capacity

T = temperature

S° = standard entropy

H° = standard enthalpy

G° = standard free energy

n = number of moles

E° = standard reduction potential

I = current (amperes)

q = charge (coulombs)

t = time (seconds)

Faraday's constant, $F = 96,485$ coulombs per mole of electrons

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$



KINETICS

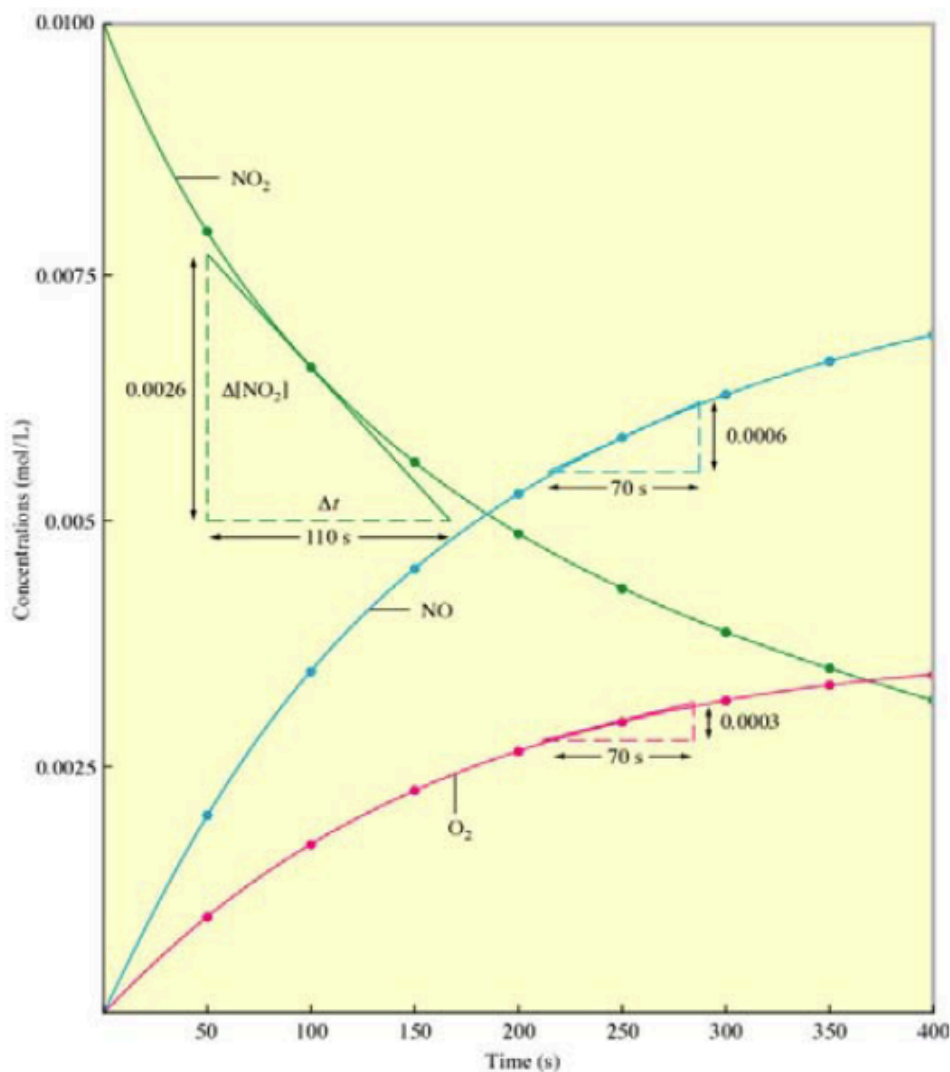
Integrated Rates — Putting it All Together

What I Absolutely Have to Know to Survive the AP Exam

The following might indicate the question deals with kinetics: rate; reactant concentration; order; rate constant; mechanisms; rate determining step; intermediate; catalyst; half-life; instantaneous rate; relative rate; activation energy; integrated rate law; rate expression; rate law

Instantaneous Rate

Instantaneous rate is the rate at any one point in time during the experiment. To find instantaneous reaction rate you find the slope of the curve at the time in question (for those of you in calculus aka...derivative) i.e. the slope of the tangent line to that point in time.



Integrated Rate – Concentration and Time

Where the differential rate law expresses rate as a function of reactant concentration(s) at an instant in time (hence instantaneous rate), **integrated rates** express the reactant concentrations as a function of time.

To solve integrated rate problems, construct a graph with time on the x -axis and then make 3 plots where the y -axis is

- Concentration of A $[A]$ vs. t
- Natural log of the concentration of A $\ln [A]$ vs. t
- Reciprocal of $[A]$ $\frac{1}{[A]}$ vs. t

LINEAR IS THE WINNER

- Zero Order reaction are linear for $[A]$ vs. t
- First Order reactions are linear for $\ln [A]$ vs. t
- Second Order reactions are linear for $\frac{1}{[A]}$ vs. t

Think $y = mx + b$

It is imperative that you can determine reaction order simply by analyzing a graph.

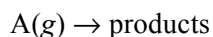
What is important?

- What is plotted on each axis?
- What does the slope of the line indicate?

If you know this, the order and rate constant can easily be determined.

Zero Order Reactions

For the reaction...



$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]_0$$

When this relationship is integrated from t to t_t then...

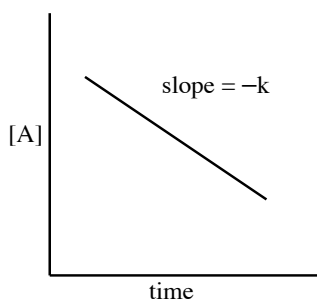
$$[A]_t = -kt + [A]_0$$

$$y = mx + b$$

Where...

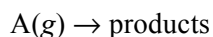
- $[A]_t$ is the concentration at time t – $[A]_t$ represents what is plotted on the y -axis
- $[A]_0$ is the initial concentration
- t is the time – represent what is plotted on the x -axis
- k is the rate constant - which is the SLOPE of the graph!
- Notice that in this equation k has a negative sign; thus the SLOPE of the graph is negative not the rate constant

If the reaction is zero order then the graph will be linear with a negative slope.



First Order Reactions

For the reaction...



$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^1$$

When this relationship is integrated from t to t_f then...

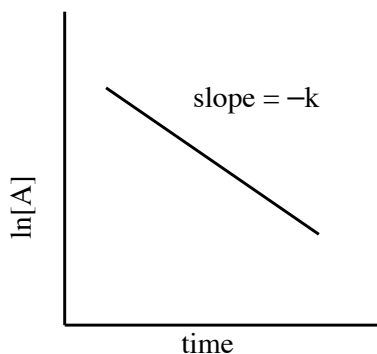
$$\ln [A]_t = -kt + \ln [A]_0$$

$$y = mx + b$$

Where...

- $[A]_t$ is the concentration at time t – $\ln [A]_t$ represents what is plotted on the y -axis
- $[A]_0$ is the initial concentration
- t is the time – represent what is plotted on the x -axis
- k is the rate constant – which is the SLOPE of the graph!
- Notice that in this equation k has a negative sign; thus the SLOPE of the graph is negative not the rate constant

If the reaction is first order then the graph will be linear with a negative slope.



Half life...

- the time required for the initial concentration, $[A]_0$, to decrease to $\frac{1}{2}$ of its value.

$$\ln [A]_t = -kt + \ln [A]_0$$

$$\ln 1 = -kt + \ln 2$$

$$\ln \frac{1}{2} = -kt$$

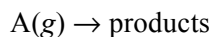
$$-0.693 = -kt$$

$$\frac{0.693}{k} = t$$



Second Order Reactions

For the reaction...



$$\text{rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$$

When this relationship is integrated from t to t_t then...

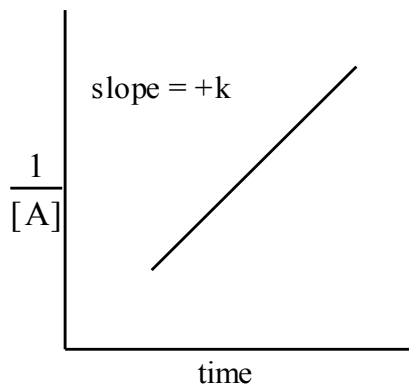
$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$$y = mx + b$$

Where...

- $[A]_t$ is the concentration at time t – $\frac{1}{[A]}$ represents what is plotted on the y -axis
- $[A]_0$ is the initial concentration
- t is the time – represent what is plotted on the x -axis
- k is the rate constant – which is the SLOPE of the graph!
- Notice that in this equation k is positive; thus the SLOPE of the graph is positive

If the reaction is 2nd order then the graph will be linear with a **positive** slope.





Kinetics Cheat Sheet

Relationships

Differential Rate Law (concentration vs. rate data):	Rate = $k [A]^x[B]^y$	
Integrated Rate Laws (concentration vs. time data):	Zero order	$[A] = (-)kt + [A]_0$
	First order	$\ln [A] = (-)kt + \ln[A]_0$
	Second order	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
$t_{1/2} = \frac{0.693}{k}$ for first order reactions and all nuclear decay		

Connections

Stoichiometry – “using up” one component of the system might indicate a limiting reactant in effect	Electrochemistry – if reaction is redox in nature, rate problems could come into play
Thermochemistry – E_a and $\Delta H^\circ_{\text{rxn}}$ and reaction diagrams	

Potential Pitfalls

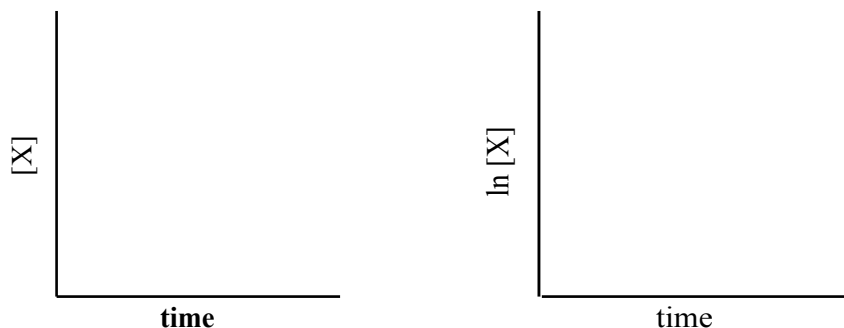
Units on k ! Make sure you can solve for units for k



NMSI SUPER PROBLEM

The decomposition of substance X was experimentally observed at 25°C and shown to be first order with respect to X. Data from the experiment are shown below.

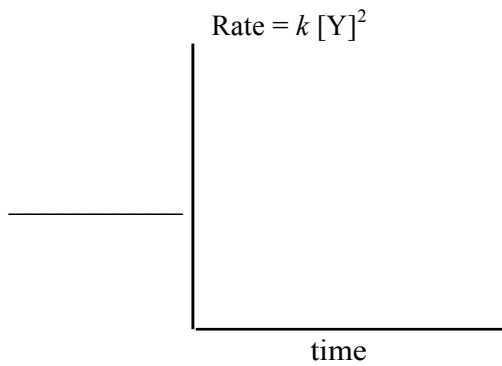
[X] M	Time (min)
0.100	0
0.088	2
0.069	6
0.054	10
0.043	14
0.030	???



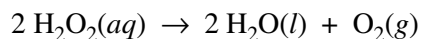
- (a) For each of the graphs above
- Sketch the expected curve based on the labeled axes. You do not need to plot the exact data.
 - Write the rate law for the decomposition of substance X.
 - Explain how one of the two graphs above can be used to determine the rate constant, k . Be sure to specify which graph.
- (b) Based on the above data
- Calculate the rate constant for this reaction. Be sure to include units.
 - How many minutes will it take for $[X]$ to become 0.030 M?



In a different experiment, the decomposition of substance Y at 50°C was determined to have the following rate law.



- (c) On the axes above
- i. Sketch the graph that is expected to provide a linear relationship when plotted against time. Be sure to label the y-axis.
 - ii. What does the slope of this line represent?
- (d) The temperature of this reaction was increased from 50°C to 100°C. Predict the effect this would have on each of the following.
- i. Rate of the reaction
 - ii. Rate constant, k
- (e) Sketch the graph of the reaction at 100°C on the plot in part (c)

2004 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

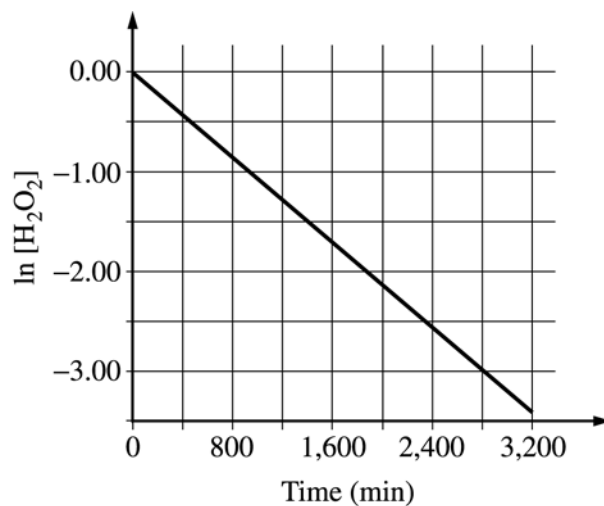
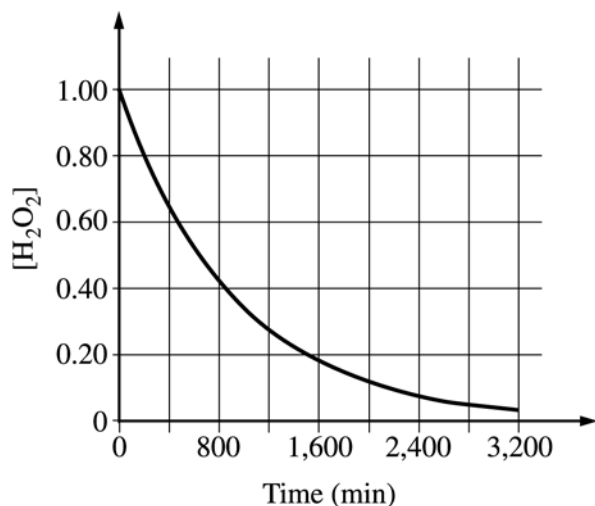
3. Hydrogen peroxide decomposes according to the equation above.

(a) An aqueous solution of H_2O_2 that is 6.00 percent H_2O_2 by mass has a density of 1.03 g mL^{-1} . Calculate each of the following.

(i) The original number of moles of H_2O_2 in a 125 mL sample of the 6.00 percent H_2O_2 solution

(ii) The number of moles of $\text{O}_2(g)$ that are produced when all of the H_2O_2 in the 125 mL sample decomposes

(b) The graphs below show results from a study of the decomposition of H_2O_2 .

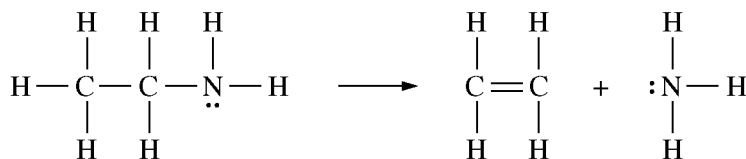


(i) Write the rate law for the reaction. Justify your answer.

(ii) Determine the half-life of the reaction.

(iii) Calculate the value of the rate constant, k . Include appropriate units in your answer.

(iv) Determine $[\text{H}_2\text{O}_2]$ after 2,000 minutes elapse from the time the reaction began.

2012 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS

3. A sample of $\text{CH}_3\text{CH}_2\text{NH}_2$ is placed in an insulated container, where it decomposes into ethene and ammonia according to the reaction represented above.

Substance	Absolute Entropy, S° , in $\text{J}/(\text{mol}\cdot\text{K})$ at 298 K
$\text{CH}_3\text{CH}_2\text{NH}_2(\text{g})$	284.9
$\text{CH}_2\text{CH}_2(\text{g})$	219.3
$\text{NH}_3(\text{g})$	192.8

- (a) Using the data in the table above, calculate the value, in $\text{J}/(\text{mol}_{\text{rxn}}\cdot\text{K})$, of the standard entropy change, ΔS° , for the reaction at 298 K.
- (b) Using the data in the table below, calculate the value, in $\text{kJ}/\text{mol}_{\text{rxn}}$, of the standard enthalpy change, ΔH° , for the reaction at 298 K.

Bond	C–C	C = C	C–H	C–N	N–H
Average Bond Enthalpy (kJ/mol)	348	614	413	293	391

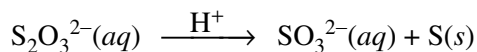
- (c) Based on your answer to part (b), predict whether the temperature of the contents of the insulated container will increase, decrease, or remain the same as the reaction proceeds. Justify your prediction.

An experiment is carried out to measure the rate of the reaction, which is first order. A 4.70×10^{-3} mol sample of $\text{CH}_3\text{CH}_2\text{NH}_2$ is placed in a previously evacuated 2.00 L container at 773 K. After 20.0 minutes, the concentration of the $\text{CH}_3\text{CH}_2\text{NH}_2$ is found to be 3.60×10^{-4} mol/L.

- (d) Calculate the rate constant for the reaction at 773 K. Include units with your answer.
- (e) Calculate the initial rate, in $M \text{ min}^{-1}$, of the reaction at 773 K.
- (f) If $\frac{1}{[\text{CH}_3\text{CH}_2\text{NH}_2]}$ is plotted versus time for this reaction, would the plot result in a straight line or would it result in a curve? Explain your reasoning.

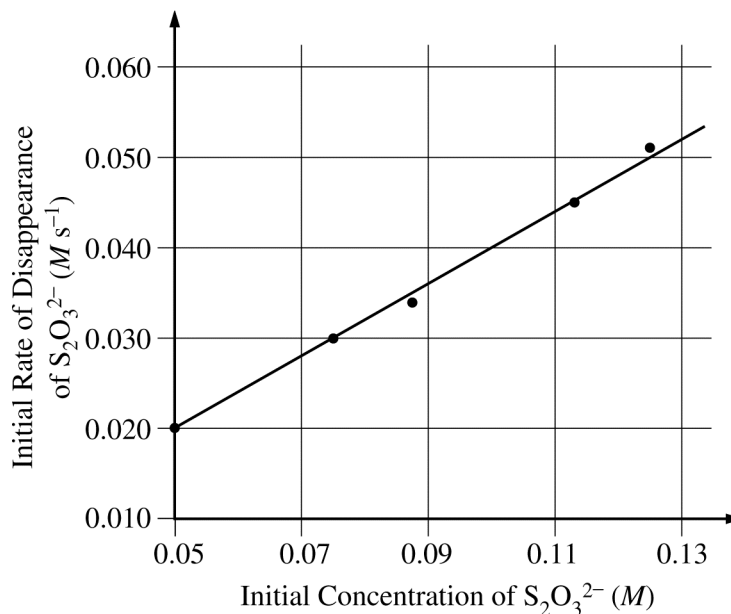
STOP

**If you finish before time is called, you may check your work on this part only.
Do not turn to the other part of the test until you are told to do so.**

2009 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS (Form B)

2. A student performed an experiment to investigate the decomposition of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, in acidic solution, as represented by the equation above. In each trial the student mixed a different concentration of sodium thiosulfate with hydrochloric acid at constant temperature and determined the rate of disappearance of $\text{S}_2\text{O}_3^{2-}(\text{aq})$. Data from five trials are given below in the table on the left and are plotted in the graph on the right.

Trial	Initial Concentration of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ (M)	Initial Rate of Disappearance of $\text{S}_2\text{O}_3^{2-}(\text{aq})$ (M s^{-1})
1	0.050	0.020
2	0.075	0.030
3	0.088	0.034
4	0.112	0.045
5	0.125	0.051



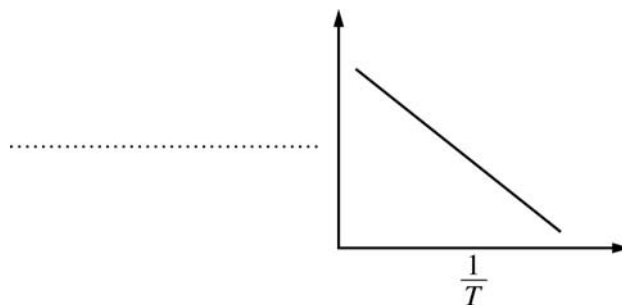
- Identify the independent variable in the experiment.
- Determine the order of the reaction with respect to $\text{S}_2\text{O}_3^{2-}$. Justify your answer by using the information above.
- Determine the value of the rate constant, k , for the reaction. Include units in your answer. Show how you arrived at your answer.
- In another trial the student mixed 0.10 M $\text{Na}_2\text{S}_2\text{O}_3$ with hydrochloric acid. Calculate the amount of time it would take for the concentration of $\text{S}_2\text{O}_3^{2-}$ to drop to 0.020 M .
- On the graph above, sketch the line that shows the results that would be expected if the student repeated the five trials at a temperature lower than that during the first set of trials.

2004 AP[®] CHEMISTRY FREE-RESPONSE QUESTIONS

3. The first-order decomposition of a colored chemical species, X, into colorless products is monitored with a spectrophotometer by measuring changes in absorbance over time. Species X has a molar absorptivity constant of $5.00 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$ and the path length of the cuvette containing the reaction mixture is 1.00 cm. The data from the experiment are given in the table below.

[X] (M)	Absorbance	Time (min)
?	0.600	0.0
4.00×10^{-5}	0.200	35.0
3.00×10^{-5}	0.150	44.2
1.50×10^{-5}	0.075	?

- (a) Calculate the initial concentration of the colored species.
- (b) Calculate the rate constant for the first-order reaction using the values given for concentration and time. Include units with your answer.
- (c) Calculate the number of minutes it takes for the absorbance to drop from 0.600 to 0.075.
- (d) Calculate the half-life of the reaction. Include units with your answer.
- (e) Experiments were performed to determine the value of the rate constant for this reaction at various temperatures. Data from these experiments were used to produce the graph below, where T is temperature. This graph can be used to determine the activation energy, E_a , of the reaction.
- (i) Label the vertical axis of the graph.
- (ii) Explain how to calculate the activation energy from this graph.



S T O P

**If you finish before time is called, you may check your work on this part only.
Do not turn to the other part of the test until you are told to do so.**