page 17-18

1 a) [NO]

$$\frac{1.0\times10^{-4}}{2.5\times10^{-5}} = \frac{[.020]^n}{[.010]^n}$$

$4 = 2^n$

$\boxed{n=2}$

$[O_2]$

$$\frac{5.0\times10^{-5}}{2.5\times10^{-5}} = \frac{[.020]^m}{[.010]^m}$$

$2 = 2^m$

$\boxed{m=1}$

b) $Rate = k[NO]^2[O_2]$

$2.5\times10^{-5}\ M/s = k[0.010]^2[.010]$

$k = 25\ M^{-2}s^{-1}$

$\boxed{Rate = 25M^{-2}s^{-1}[NO]^2[O_2]}$

c) $k = 25\ M^{-2}s^{-1}$ (see above)

d) $Rate = (25)(.015)^2(.0050)$

$\boxed{Rate = 2.8\times10^{-5}\ M/s}$

e) O_2 is going half as fast as NO

$(1.0\times10^{-4})/2 = \boxed{+5.0\times10^{-5}\ M/s}$

NO_2 is going at the same rate as NO

$\boxed{1.0\times10^{-4}\ M/s}$

(2) a) [NO]

$$\frac{.136}{.0339} = \frac{[.420]^n}{[.210]^n}$$

$$4 = 2^n$$

$$\boxed{n = 2}$$

$[H_2]$

$$\frac{.0678}{.0339} = \frac{[.244]^m}{[.122]^m}$$

$$2 = 2^m$$

$$\boxed{m = 1}$$

b) $Rate = k[NO]^2[H_2]$

c) $.136 = k[.420]^2[.122]$

$$\boxed{k = 6.32\ M^{-2}s^{-1}}$$

d) $Rate = (6.32)(0.350\,M)^2(.205)$

$$\boxed{Rate = .159\ M/s}$$

(3) a)

$$\frac{4.0\times10^{-6}}{2.0\times10^{-6}} = \frac{[1.0\times10^{-1}]^n}{[5.0\times10^{-2}]^n}$$

$$2 = 2^n$$

$$\boxed{n = 1}$$

b)

$$\frac{2.0\times10^{-6}}{2.0\times10^{-6}} = \frac{[4.0\times10^{-2}]^m}{[2.0\times10^{-2}]^m}$$

$$1 = 2^m$$

$$\boxed{m = 0}$$

c) 1st

d) $Rate = k[(CH_3)_3CBr]$

e) $(2.0\times10^{-6}) = k(5.0\times10^{-2})$

$k = 4.0\times10^{-5}\ 1/s$

Worksheet 12.6a Integrated Rate Law Name________________________

1. The decomposition of hydrogen peroxide was studied, and the following data was obtained at a particular temperature.
Rate = $-\Delta[H_2O_2]/\Delta t$

Time (s)	$[H_2O_2]$ (mol/L)
0	1.00
120	0.91
300	0.78
600	0.59
1200	0.37
1800	0.22
2400	0.13
3000	0.082
3600	0.050

a. Determine the rate law

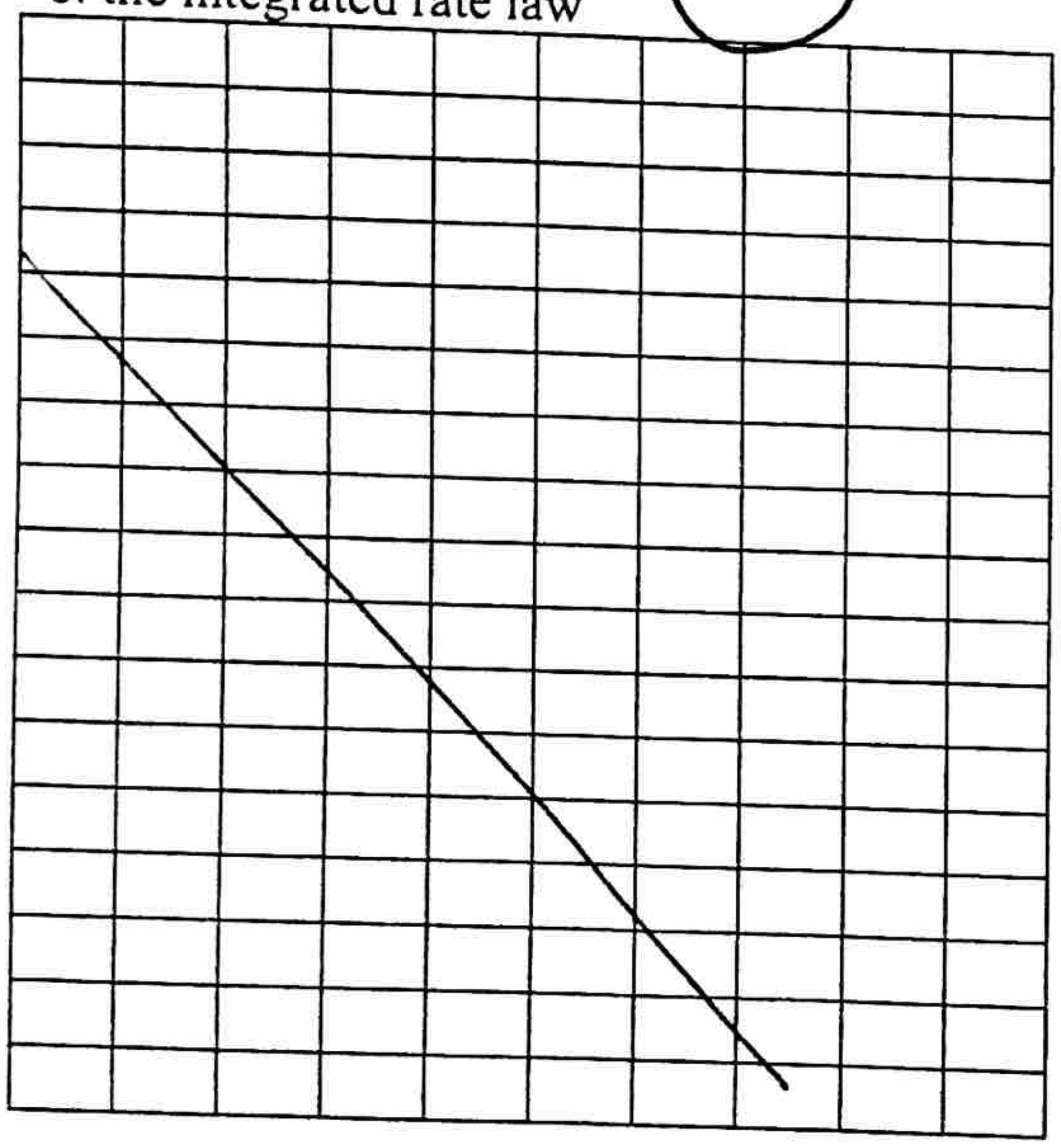
$\cancel{\ln[A] = -kt + \ln[A]_0}$

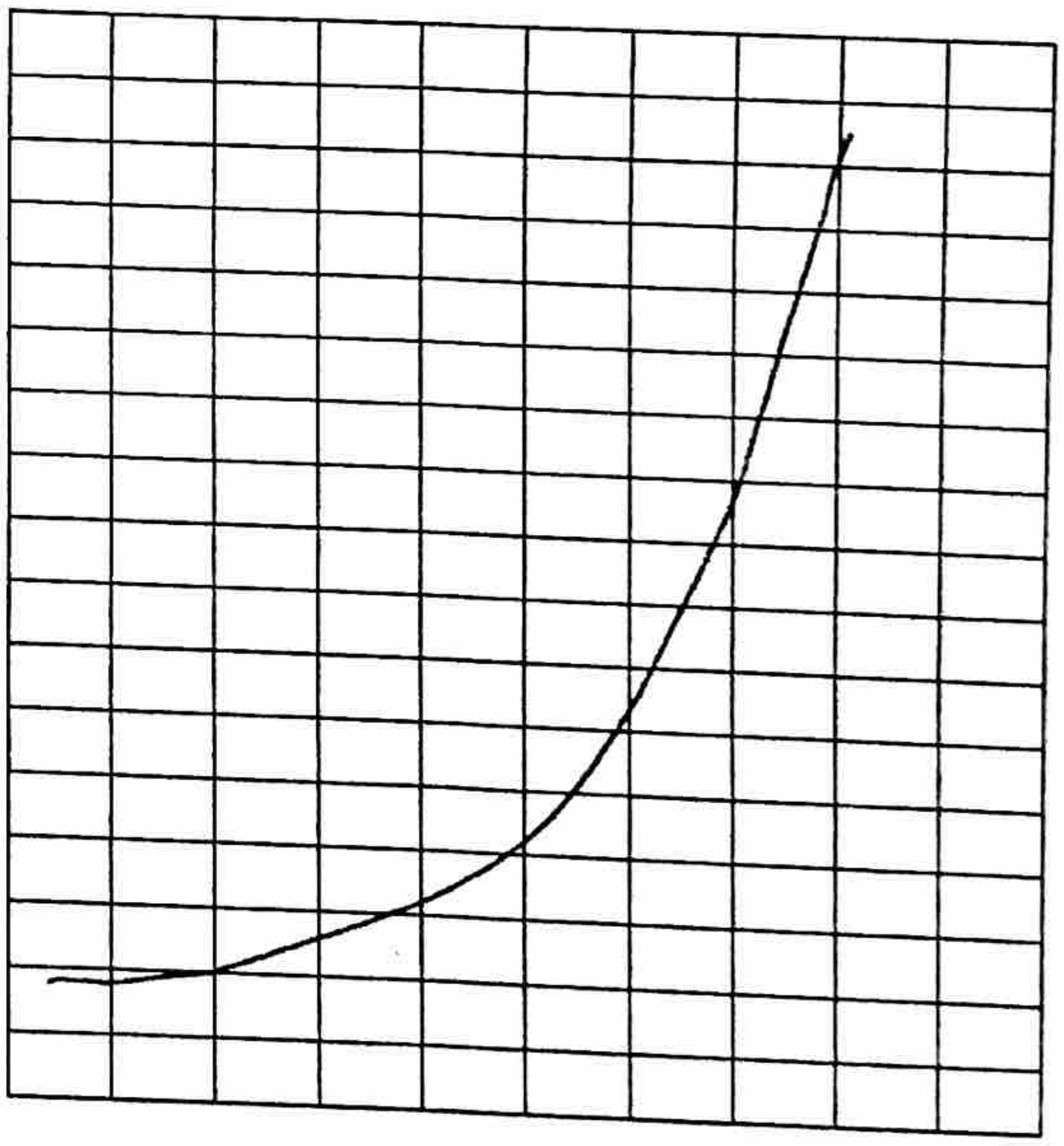
Rate = $k[H_2O_2]$

1st

2nd

b. the integrated rate law





c. the value of the rate constant

$k = 8.3\times10^{-4}\ s^{-1}$ (slope)

d. Calculate the $[H_2O_2]$ at 4000. s after the start of the reaction

$\ln[A] = -8.3\times10^{-4}\ s^{-1}(4000.\ s) + \ln(1)$

$\ln[A] = -3.32$

$e \qquad e$

$\boxed{[A] = .036\ M}$

27

Worksheet 12.6b Integrated Rate Law   Name________________________

2. If The rate of the reaction : $NO_2 + CO \rightarrow NO + CO_2$ depends only on the concentration of nitrogen dioxide below 225 C. At a temperature below 225 C, the following data was collected:

Time (s)	$[NO_2]$ (mol/L)
0	0.500
1.20×10^3	0.444
3.00×10^3	0.381
4.50×10^3	0.340
9.00×10^3	0.250
1.80×10^4	0.174

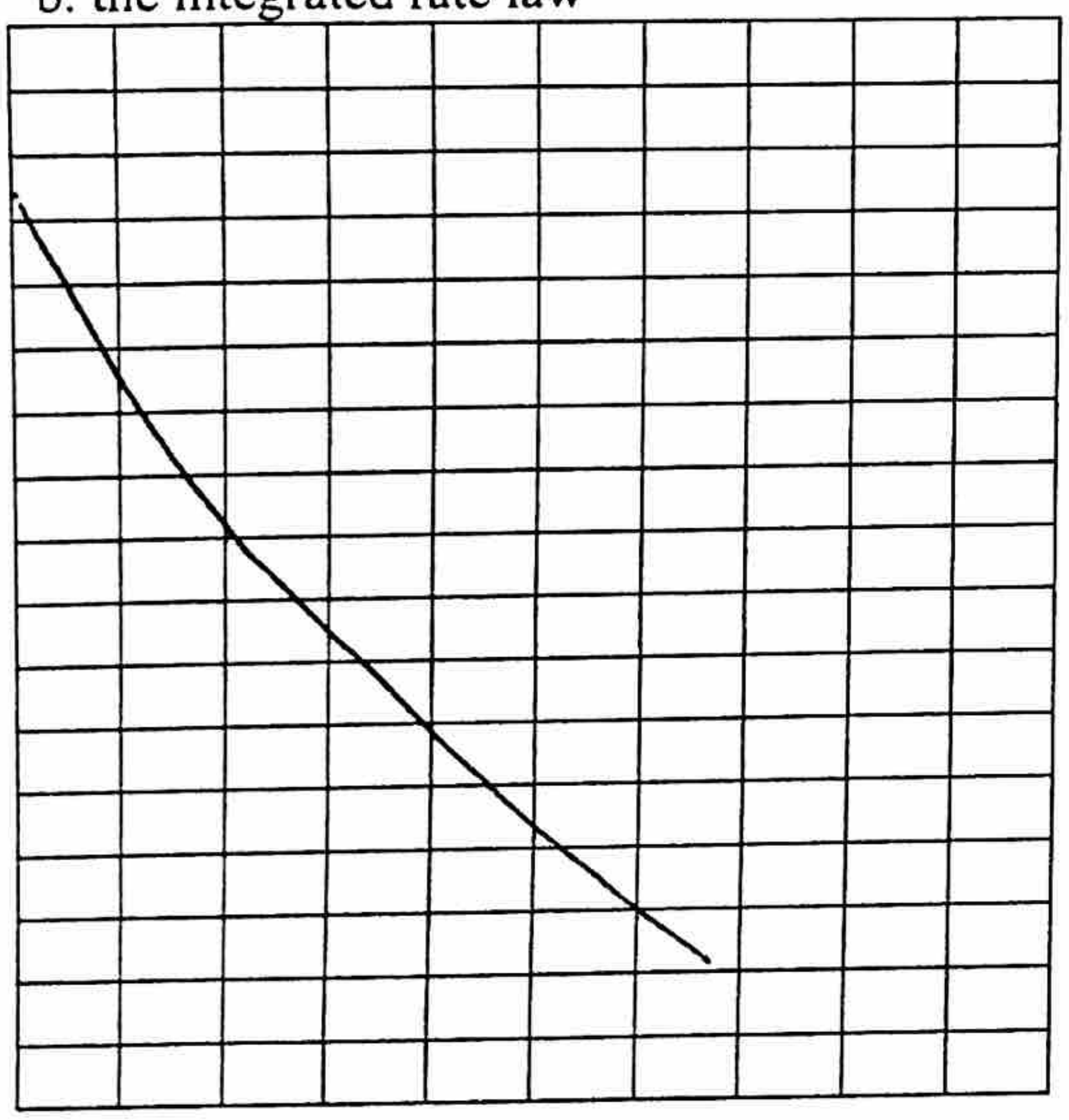
a. Determine that rate law

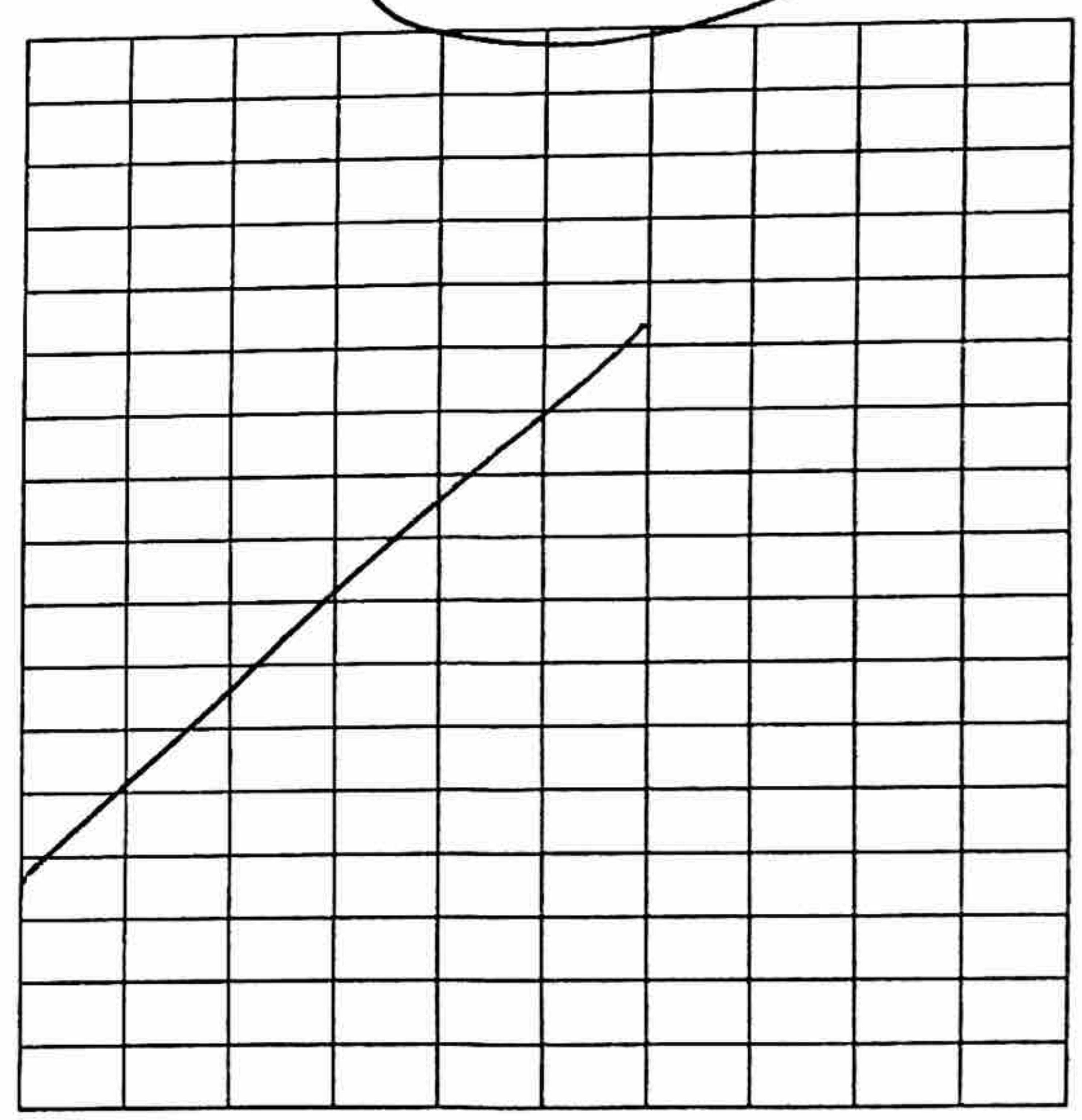
Rate = $k[NO_2]^2$

1st order

2nd order

b. the integrated rate law





c. the value of the rate constant.

$$\frac{1}{.444} = k(1.20 \times 10^3) + \frac{1}{.5}$$

$$\boxed{K = 2.1 \times 10^{-4}\ M^{-1}s^{-1}}$$

d. Calculate the $[NO_2]$ at 2.70×10^4 s after the start of the reaction

$$\frac{1}{X} = (2.1 \times 10^{-4}\ M^{-1}s^{-1})(2.70 \times 10^4) + \frac{1}{.5}$$

$$\frac{1}{X} = 7.67 \qquad X = .130\ M$$

3. A certain first-order reaction is 45.0 % complete in 65 s. What are the rate constant and the half-life for this process?

$$\ln(55) = -k(65s) + \ln(100)$$

$$K = .0092\ s^{-1}$$

$$t_{1/2} = \frac{\ln(2)}{.0092\ s^{-1}}$$

$$t_{1/2} = 75\ s$$

28

Worksheet 12.6c Integrated Rate Law Name________________________

4.A certain reaction has the following general form: aA → bB
At a particular temperature and $[A]_0 = 2.00 \times 10^{-2}$ M, Concentration vs. time data were collected for this reaction, and a plot of ln[A] vs. time resulted in a straight line with a slope value of -2.97×10^{-2} min^{-1}.

a. Determine the rate law.

Rate = k[A]

b. Determine the integrated rate law

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

c. Determine the rate constant for this reaction.

2.97×10^{-2} min^{-1} (slope)

d. Calculate the half-life for this reaction

$t_{1/2} = \frac{\ln(2)}{-2.97 \times 10^{-2}} = 23.3$ min

e. How much time is required for the concentration of A to decrease to 2.50×10^{-3}M?

$\ln(2.50 \times 10^{-3} M) = -(2.97 \times 10^{-2} min^{-1})(t) + \ln(2.00 \times 10^{-2})$

* subtracting ln is really dividing*

t = 70.0 min

5. The radioactive isotope ^{32}P decays by first-order kinetics and has a half-life of 14.3 days. How long does it take for 95.0 % of a sample of ^{32}P to decay?

$t_{1/2} = \frac{\ln(2)}{k}$

$14.3 \text{ days} = \frac{\ln(2)}{k}$

k = 0.0485

$\ln(5) = -0.0485t + \ln(100)$

$-2.996 = -.0485t$

t = 61.8 days

6. The rate law for the decomposition of NOBr is Rate = $k[NOBr]^2$. a. If the half-life for this reaction is 2.00 s when $[NOBr]_0 = 0.900$ M, calculate the value of k for this reaction. B. How much time is required for the concentration of NOBr to decrease to 0.100M?

*2nd order

a) $t_{1/2} = \frac{1}{k(A_0)}$

$2.00s = \frac{1}{k(.900)}$

$1.8k = 1$

$k = .556 s^{-1}$

b) $\frac{1}{.100 M} = .556t + \frac{1}{.900}$

$10 = .556t + 1.11$

t = 16.0 s

29

Worksheet 12.7 Reaction Mechanisms

Name____________________________

1. Write the rate laws for the following elementary reactions:

$CH_3NC \rightarrow CH_3CN$

Rate = k[CH_3NC]

$O_3 + NO \rightarrow O_2 + NO_2$

Rate = k·[O_3][NO]

$O_3 \rightarrow O + O_2$

Rate = k[O_3]

$O_3 + O \rightarrow 2O_2$

Rate = k[O_3][O]

2. The proposed mechanism for a reaction is:

$C_4H_9Br \rightarrow C_4H_9^+ + Br^{-1}$ Slow

$C_4H_9^+ + H_2O \rightarrow C_4H_9OH_2^+$ Fast

$C_4H_9OH_2^+ + H_2O \rightarrow C_4H_9OH + H_3O^+$ Fast

$C_4H_9Br + 2H_2O \rightarrow Br^- + C_4H_9OH + H_3O^+$

Write the rate law expected for this mechanism. What is the overall balanced equation for the reaction? What are the intermediates in the proposed mechanism?

Rate law

Rate = k[C_4H_9Br]

Balanced Reaction

$C_4H_9Br + 2H_2O \rightarrow Br^- + C_4H_9OH + H_3O^+$

Intermediates

$C_4H_9^+$, $C_4H_9OH_2$

3. The mechanism for the reaction of nitrogen dioxide with carbon monoxide to form nitric dioxide and carbon dioxide is thought to be:

$NO_2 + \cancel{NO_2} \rightarrow \cancel{NO_3} + NO$ Slow

$\cancel{NO_3} + CO \rightarrow \cancel{NO_2} + CO_2$ Fast

Write the rate law expected for this mechanism. What is the overall balanced equation for the reaction?

Rate = k[NO_2]^2

$NO_2 + CO \rightarrow NO + CO_2$

30