

1. For the reaction between nitrogen(II) oxide and chlorine to produce nitrosyl chloride, $2NO + Cl_2 \rightarrow 2NOCl$, it is found that tripling the concentration of both reactants increases the rate by a factor of 27. If only the concentration of chlorine is tripled, the rate increases by a factor of 3. The order of this reaction with respect to NO is

- a. 0.
b. 1/2.
c. 1.
d. 2.
e. 3.

$$\text{rate} = k [NO]^x [Cl_2]^y$$

When tripled (Both) $[3]^x [3]^y = 27$

When $[1]^x [3]^y = 3$ so $y = 1$
and $x = 2$

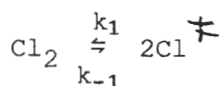
2. The rate constants for the decomposition of a compound are $6.2 \times 10^{-4} \text{ s}^{-1}$ at 45°C and $2.1 \times 10^{-3} \text{ s}^{-1}$ at 55°C . What is the value of the activation energy for this reaction in kJ/mol ?

- a. 46
b. 1.1×10^2
c. 2.5×10^3
d. 2.5×10^4
e. 1.1×10^5

$$\ln\left(\frac{6.2 \times 10^{-4}}{2.1 \times 10^{-3}}\right) = \frac{E_a}{8.314 \text{ J/mol}\cdot\text{K}} \left(\frac{1}{55+273} - \frac{1}{45+273}\right)$$

$$E_a = 105794 \text{ J/mol} = 1.1 \text{ kJ/mol}$$

3. The reaction $CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$ has been proposed to occur by the mechanism

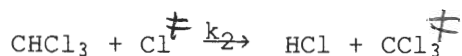


fast equilibrium

$$\text{rate for} = \text{rate rev}$$

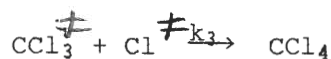
$$k_1 [Cl_2] = k_{-1} [Cl^\ddagger]^2$$

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



slow step

$$\text{rate} = k_2 [CHCl_3] [Cl^\ddagger]$$



very fast equilibrium

$$\text{rate} = k_2 [CHCl_3] \sqrt{\frac{k_1 [Cl_2]}{k_{-1}}}$$

The overall experimental rate law which is consistent with this mechanism is

- a. $\text{rate} = k_1 [Cl_2]$
b. $\text{rate} = k_2 [CHCl_3] [Cl]$
c. $\text{rate} = k_3 [CCl_3] [Cl]$
d. $\text{rate} = k_{\text{exp}} [CHCl_3] [Cl_2]$
e. $\text{rate} = k_2 k_{\text{eq}} [CHCl_3] [Cl_2]^{1/2}$

$$\text{rate} = k [CHCl_3] [Cl_2]^{1/2}$$

4. Most reactions are more rapid at high temperatures than at low temperatures. This is consistent with which of the following?

1. an increase in the rate constant with increasing temperature
2. an increase in the activation energy with increasing temperature
3. an increase in the percentage of "high-energy" collisions with increasing temperature

- a. 1 only
b. 2 only
c. 3 only
d. 1 and 3
e. 1, 2, and 3

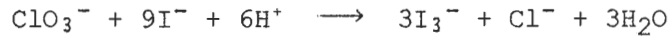
5. A reaction which is second order in one reactant has a rate constant of $1.0 \times 10^{-1} \text{ L mol}^{-1} \text{ s}^{-1}$. If the initial concentration of the reactant is 0.100 M , how long will it take for the concentration to become 0.0500 M ?

- a. 100 s**
b. 500 s
c. 1000 s
d. 1500 s
e. 10,000 s

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

$$\frac{1}{0.0500} = (1.0 \times 10^{-1})t + \frac{1}{0.100}$$

6. The rate law for the oxidation of the iodide ion by the chlorate ion in aqueous acidic solution,



has been found to be

$$\text{Rate} = k[\text{ClO}_3^-][\text{I}^-][\text{H}^+]^2$$

The overall order for the reaction is

- a. 1.
- b. 2.
- c. 4.
- d. 9.
- e. 16.

7. ⁶⁴Co decays by a first-order process via the emission of a beta particle. The ⁶⁴Co isotope has a half-life of 7.8 min. How long will it take for 15/16 of the cobalt to undergo decay?

- a. 7.8 min
- b. 15.6 min
- c. 23.4 min
- d. 31.2 min
- e. 39.0 min

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

$$\ln\left[\frac{1}{16}\right] = (-8.89 \times 10^{-2} \text{ min}^{-1})t$$

$$t = 31.2 \text{ min}$$

↳ 1/16 left

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{7.8} = 8.89 \times 10^{-2} \text{ min}^{-1}$$

8. The rate of reaction is usually expressed as the change in

- a. the activation energy upon the addition of a catalyst.
- b. the equilibrium expression upon the addition of a catalyst.
- c. the pH at the equivalence point.
- d. concentration per unit time.
- e. concentration of the reactants versus that of the products.

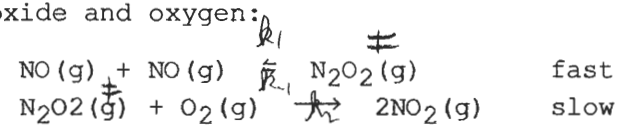
9. A catalyst speeds up a chemical reaction by

- a. changing the stoichiometry.
- b. increasing the activation energy.
- c. providing an alternate reaction mechanism.
- d. shifting the equilibrium.
- e. increasing the reaction enthalpy.

10. All of the following would be expected to affect the rate of a chemical reaction except

- a. adding more reactants.
- b. removing some products.
- c. increasing the temperature.
- d. decreasing the temperature.
- e. adding a catalyst.

11. The following mechanism has been suggested for the reaction between nitrogen dioxide and oxygen:



$$k_1[\text{NO}]^2 = k_{-1}[\text{N}_2\text{O}_2]$$

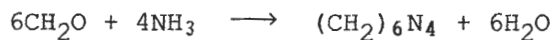
$$\text{rate} = k_2[\text{N}_2\text{O}_2][\text{O}_2]$$

According to this mechanism the experimental rate law is

- a. second order in NO and zero order in O₂.
- b. second order in NO and first order in O₂.
- c. first order in NO and first order in O₂.
- d. first order in NO and second order in O₂.
- e. first order in NO and zero order in O₂.

$$\text{rate} = \frac{k_1 k_2}{k_{-1}} [\text{NO}]^2 [\text{O}_2]$$

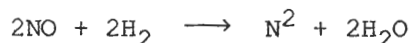
12. For the reaction



the rate is expressed as $\frac{1}{6} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$. An equivalent expression is

- a. $\frac{1}{2} \frac{\Delta[(\text{CH}_2)_6\text{N}_4]}{\Delta t}$ ✓
- b. $6 \frac{\Delta[\text{CH}_2\text{O}]}{\Delta t}$ ✓
- c. $-6 \frac{\Delta[\text{CH}_2\text{O}]}{\Delta t}$ ✓
- d. $-\frac{1}{4} \frac{\Delta[\text{NH}_3]}{\Delta t}$ ✓
- e. $-\frac{1}{6} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$ ✗

13. Nitric oxide reacts with hydrogen at a measurable rate at 1000 K according to the equation



The experimental rate law is

$$\text{Rate} = k [\text{NO}]^2 [\text{H}_2]$$

When time is in minutes and the concentration is in moles per liter, the units for k are

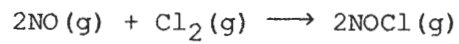
- a. $\frac{\text{moles}}{\text{L} \cdot \text{min}}$
- b. $\frac{\text{moles}}{\text{L} \cdot \text{min}}$
- c. $\frac{\text{L}^2}{\text{moles}^2 \cdot \text{min}}$ ✓
- d. $\frac{\text{moles}^2}{\text{L}^2 \cdot \text{min}}$
- e. $\frac{\text{moles}^3}{\text{L}^3 \cdot \text{min}}$

$$\frac{\text{M}}{\text{min}} = \frac{\text{M}^2 \cdot \text{M}}{\text{min M}^2}$$

14. Which of the following statements is always true?

- a. Exothermic reactions have lower activation energies than endothermic reactions.
- b. The rate for a reaction depends on the concentrations of all the reactants.
- c. The rate of a catalyzed reaction is dependent on the concentration of the catalyst. ✓
- d. The specific rate constant is dependent on the concentrations of the reacting species.
- e. The rate law can be determined from the stoichiometric equation.

15. Nitrosyl chloride is produced from the reaction of nitrogen(II) oxide and chlorine.



The following initial rates at a given temperature were obtained for the concentrations listed below:

Experiment	Rate $\frac{\text{mol}}{\text{L} \cdot \text{hr}}$	NO $\frac{\text{mol}}{\text{L}}$	Cl ₂ $\left[\frac{\text{mol}}{\text{L}}\right]$
1	2.21	0.25	0.25
2	8.83	0.50	0.25
3	17.5	0.50	0.50

For NO: $\frac{8.83}{2.21} = \left(\frac{0.50}{0.25}\right)^x$

$4 = 2^x$
 $x = 2$

for Cl₂: $\frac{17.5}{8.83} = \left(\frac{0.50}{0.25}\right)^y$

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

The experimental rate law is

- a. rate = k[NO]
- b. rate = k[NO]^{1/2}[Cl₂]
- c. rate = k[NO][Cl₂]^{1/2}
- d. rate = k[NO]²[Cl₂]
- e. rate = k[NO][Cl₂]

16. In a first-order reaction the half-life is 20. minutes. The rate constant, k, in

- min⁻¹ is
- a. 0.035.
- b. 0.35.
- c. 3.5.
- d. 13.9.
- e. 35.

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

$k = \frac{0.693}{20.} \text{ min} = 0.0347 \text{ min}^{-1}$

17. For a certain second-order decomposition reaction, the rate is 0.30 mol/(L · s) when the concentration of the reactant is 0.20 M. What is the rate constant (in units L/(mol · s)) for this reaction?

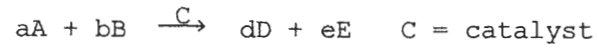
- a. 0.67
- b. 1.5
- c. 2.2
- d. 3.0
- e. 7.5

rate = k[A]²
 $\frac{0.30 \text{ M}}{\text{s}} = k[0.20]^2$
 $k = 7.5 \text{ M}^{-1} \text{ s}^{-1}$

18. The main reason for the increase in reaction rate with temperature is that

- a. heat acts as a catalyst.
- b. the activation energy increases rapidly with temperature.
- c. a 10° temperature rise results in the rate doubling.
- d. there is a dramatic increase in the number of collisions.
- e. the fraction of high-energy molecules increases exponentially with temperature.

19. Consider the reaction



The rate law is

$$\text{Rate} = k[\text{A}]^q[\text{B}]^r[\text{C}]^s$$

Which of the following statements is false?

- a. The exponents q, r, and s are often integers.
- b. The exponents q and r are always equal to the coefficients a and b, respectively.
- c. The exponent s must be determined experimentally.
- d. The symbol k represents the rate constant.
- e. The overall reaction order is q + r + s.

The times listed in the following table are those required for the concentration of $S_2O_8^{2-}$ to decrease by 0.00050 M as measured in an "iodine clock" reaction at 23°C. The net reaction is



Experiment	$[S_2O_8^{2-}]_0$	$[I^-]_0$	Time (sec)	Relative Rate $\frac{\Delta[M]}{\Delta t}$
I	0.0400	0.0800	39	1.28×10^{-5}
II	0.0400	0.0400	78	6.41×10^{-6}
III	0.0100	0.0800	156	3.21×10^{-6}
IV	0.0200	0.0200	?	?

Convert to
from $\frac{0.00050 M}{39 \text{ Sec}}$

Calculate the expected time in seconds for experiment IV.

- a. 634
- b. 312**
- c. 234
- d. 156
- e. 78

for order wrt. $(S_2O_8^{2-})$: $\frac{1.28 \times 10^{-5}}{3.21 \times 10^{-6}} = \left(\frac{0.0400}{0.0100}\right)^x \quad x = 1$

for order wrt. $[I^-]$: $\frac{1.28 \times 10^{-5}}{6.41 \times 10^{-6}} = \left(\frac{0.0800}{0.0400}\right)^y \quad y = 1$

rate = $k[S_2O_8^{2-}][I^-] \rightarrow k = 0.0040 M^{-1} s^{-1}$ and see below*

21. The oxidation of ammonia produces nitrogen and water via the reaction $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$. If the rate of formation of N_2 is 2.0 mol/(L · s), then the rate at which

- a. H_2O is being formed is 2.0 mol/(L · s).
- b. NH_3 reacts is 4.0 mol/(L · s).**
- c. O_2 reacts is 1.5 mol/(L · s).
- d. NH_3 reacts is 0.50 mol/(L · s).
- e. H_2O is being formed is 0.67 mol/(L · s).

rate = $\frac{-1/4 \Delta[NH_3]}{\Delta t} = \frac{-1/3 \Delta[O_2]}{\Delta t} = \frac{1/2 \Delta[N_2]}{\Delta t} = \frac{1/6 \Delta[H_2O]}{\Delta t}$

22. A chemical reaction that is first order in x is observed to have a rate constant of $1.2 \times 10^{-2}/s$. If the initial concentration of x is 2.0 M, what is the concentration of x after 200 s?

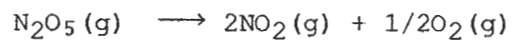
- a. 0.18 M**
- b. 0.55 M
- c. 1.0 M
- d. 6.0×10^{-3} M
- e. 1.7 M

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

$\ln[X]_t = (-1.2 \times 10^{-2})(200) + \ln[2.0]$

$\ln[X]_t = -1.707 \quad \text{so} \quad e^{-1.707} = 0.181 M$

23. The gas-phase decomposition of N_2O_5 is a first-order process with a rate constant of $1.50 \times 10^{-3}/s$ at 55°C. The decomposition reaction is



Ten (10.0) g of N_2O_5 are placed in vessel 1 and 5.0 g of N_2O_5 in vessel 2. The vessels are at the same temperature and pressure. How much time is required for half of the N_2O_5 to decompose in each vessel?

- a. Vessel 1 requires twice as much time as vessel 2.
- b. Vessel 2 requires twice as much time as vessel 1.
- c. Vessel 1 requires three times as much time as vessel 2.
- d. Vessel 1 requires four times as much time as vessel 2.
- e. Vessel 1 requires the same amount of time as vessel 2.**

1st order half life is independent of conc.

* 20. rate₃ = $0.0040 [0.0200][0.0200] = 1.6 \times 10^{-6} \frac{M}{s}$

so for time rate = $\frac{\Delta[I]}{\Delta t}$

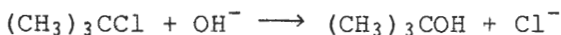
$\Delta t = \frac{0.00050}{1.6 \times 10^{-6}} = 312.5 \text{ seconds}$

24. For the reaction $I + I \rightarrow I_2$ at 25°C in CCl_4 ,

$k = 8.2 \times 10^9 \text{ L}/(\text{mol} \cdot \text{s})$. From a consideration of the rate constant, we know that the reaction is

- a. first order. since $k_{\text{unit}} = \text{M}^{-1}\text{s}^{-1}$
b. second order. so rate eq. must be $\text{rate} = k[\text{I}]^2$
 c. endothermic.
 d. One can't tell without knowing the activation energy.
 e. One can't tell without an experiment showing the concentration dependence of the iodine atom.

25. For the reaction



it is experimentally found that doubling the concentration of $(\text{CH}_3)_3\text{CCl}$ causes the reaction rate to be increased twofold, but doubling the concentration of OH^- has no effect on the rate. The rate equation is

- a. $R = k[(\text{CH}_3)_3\text{CCl}][\text{OH}^-]$.
 b. $R = k[(\text{CH}_3)_3\text{CCl}]^2[\text{OH}^-]$.
c. $R = k[(\text{CH}_3)_3\text{CCl}]$.
 d. $R = k[(\text{CH}_3)_3\text{COH}][\text{Cl}^-]$.
 e. $R = k \frac{[(\text{CH}_3)_3\text{COH}][\text{Cl}^-]}{[(\text{CH}_3)_3\text{CCl}][\text{OH}^-]}$.

for $[(\text{CH}_3)_3\text{CCl}] : [2]^x = 2$
 $x = 1$

for $[\text{OH}^-] : [2]^y = 1$
 $y = 0$

26. Consider these data in order to answer the question that follows.

[A]	[B]	[C]	Initial Rate
0.4	0.4	0.2	160
0.2	0.4	0.4	80
0.6	0.1	0.2	15
0.2	0.1	0.2	5
0.2	0.2	0.4	20

for (A): $\frac{15}{5} = \left(\frac{0.6}{0.2}\right)^x$, $3 = 3^x$, $x = 1$

for (B): $\frac{160}{5} = \left(\frac{0.4}{0.2}\right)^y \left(\frac{0.4}{0.1}\right)^z$
 $16 = (2)^y (4)^z$
 $y = 2$

What is the order of the reaction with respect to B?

- a. zero order
 b. first order
c. second order
 d. minus one
 e. impossible to tell from the data given

27. Two reactants, A and B, are mixed, and the reaction is timed until a color change occurs. The data are as follows:

	[A]	[B]	Time (sec)
1	0.100	0.140	25
2	0.050	0.140	50
3	0.100	0.070	100

* Note: Longer time means slower rxn
 so rxn 1 is 4 times faster than rxn 3

The order of the reaction in terms of [B] is

- a. 1/2.
 b. 1.
c. 2.
 d. 3.
 e. 4.

so: $\frac{4}{1} = \left(\frac{0.140}{0.070}\right)^x$
 $4 = 2^x$
 $x = 2$

28. A first-order chemical reaction is observed to have a rate constant of $25/\text{min}$. What is the corresponding half-life for the reaction?

- a. 12.5 min
 b. 17.3 min
 c. 0.29 s
d. 1.66 s
 e. 0.0277 s

$t_{1/2} = \frac{\ln 2}{25} \text{ min} = 0.0277 \text{ min}$

$0.0277 \text{ min} \times \frac{60 \text{ sec}}{1 \text{ min}} \Rightarrow 1.66 \text{ s}$

Key

29. From a consideration of the following reaction system



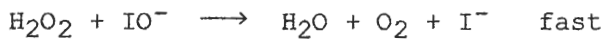
we can conclude

- a. the reaction is second order in H₂S and first order in O₂.
- b. the reaction is first order in H₂S and second order in O₂.
- c. rate = $k[\text{H}_2\text{S}]^2[\text{O}_2]$.
- d. rate = $k[\text{H}_2\text{S}][\text{O}_2]$.

e. none of these conclusions are justified.

Experiment only

30. The reaction mechanism for the decomposition of H₂O₂ is



I⁻ = catalyst

IO⁻ = intermediate

Which of the following statements is true?

- a. I⁻ is an intermediate.
- b. IO⁻ is a catalyst.
- c. The reaction is first order with respect to [I⁻].
- d. The reaction is zero order with respect to [I⁻].
- e. The reaction is second order with respect to [H₂O₂].

31. At a given temperature, a first-order reaction has a rate constant of $2.5 \times 10^{-3} \text{ s}^{-1}$

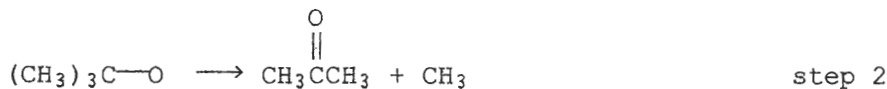
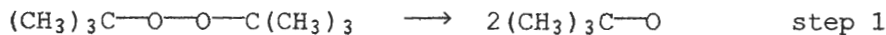
1. The time required for the reaction to be 65% completed is

- a. 75 s.
- b. 170 s.
- c. 180 s.
- d. 340 s.
- e. 420 s.

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

$$\ln(0.35) = (-2.5 \times 10^{-3})t$$

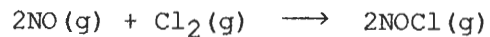
32. A mechanism that explains the rate law, rate = $k[(\text{CH}_3)_3\text{CO}_2\text{C}(\text{CH}_3)_3]$, for the gas-phase thermal decomposition of di-tert-butyl peroxide is



For this reaction the rate-determining step(s) must be

- a. step 1.
- b. step 2.
- c. step 3.
- d. 2 times step 2.
- e. step 1 + step 2 + step 3.

33. The rate law for the reaction between chlorine and nitric oxide,



is $\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$. Which of the following changes will alter the value of the specific rate constant, k ?

- a. adding more NO to the reaction system
 - b. adding more Cl_2 to the reaction system
 - c. adding more NO and Cl_2 to the reaction system
 - d. decreasing the volume of the reaction system
 - e. running the reaction in a solvent rather than in the gas phase *Changes mechanism*
34. When the concentrations of the reactants are increased, the rate of the reaction increases. This is best explained by the increase in the
- a. activation energy.
 - b. frequency of the molecular collisions.
 - c. rate constant.
 - d. kinetic energy of the molecules.
 - e. potential energy of the molecules.