AP Chemistry

Study Guide - Answers

Chapter 14

Name: ______________________

Date:________________ Per:_________

1. Define:
   a. Homogeneous reaction: ______________________
   b. Heterogeneous reaction: ______________________
   c. Activated complex: an intermediate state formed during the conversion of reactants into products – a structure that results at the maximum energy point along the reaction path
   d. Activation energy: minimum amount of energy required to initiate a reaction – amount of energy that must be added to the reactants to achieve an activated complex by breaking the bonds of the reactants
2. How is average rate of reaction calculated? rate = - Δ[reactant]/Δt or rate = Δ[product]/Δt
3. What is the relationship between Δ[product] and Δ[reactant] for a chemical reaction? Changes in concentration are related via mole ratios
4. Describe an effective collision: ______________________
5. What are three factors that affect reaction rate? Physical state of the reactants, reactant concentration, reaction temperature, presence of catalysts
6. Why is gas pressure directly related to gas concentration? As a fixed quantity of gas is pressurized, it's concentration increases proportionally via Boyle's Law (pressure increases, volume decreases causing concentration to increase)
7. Describe the method of initial rates? ______________________
8. What are two methods of determining the order of a reactant using experimental data? ______________________
9. What is an integrated rate law used for? ______________________
10. Complete the following table for integrated rate law calculations:

	Zero Order Reaction	First Order Reaction	Second Order Reaction
Rate Law Constant Unit:	M/s	1/s	1/M•s or ($M^{-1}s^{-1}$)
Integrated Rate Law:	$[A] = -kt + [A]_0$	$\ln [A] = -kt + \ln[A]_0$	$1/[A] = kt + 1/[A]_0$
½-life Formula:	$t_{1/2} = [A]_0/2k$	$t_{1/2} = \ln2/k$	$t_{1/2} = 1/k[A]_0$
y-value for Straight-Line Plot:	[A]	ln [A]	1/[A]

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How does the ½-life change over time?	Half-life decreases as concentration decreases	Half-life remains constant as concentration decreases.	Half-life increases as concentration decreases.

11. What is the relationship between reaction rate and activation energy? ____________________

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12. What is the Arrhenius equation? How do the variables affect the value? ____________________

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13. Describe a reaction mechanism: a step by step sequence of elementary reactions by which overall chemical change occurs. It describes in detail exactly what takes place at each stage of an overall chemical reaction

14. Define:
    a. Molecularity: Molecularity in chemistry is the number of molecules that come together to react in an elementary (single-step) reaction and is equal to the sum of stoichiometric coefficients of reactants in this elementary reaction.
    b. Rate-determining Step: the slowest elementary step in a reaction mechanism
    c. Initial Step: the first step in a reaction mechanism

15. Complete the following table for elementary reactions:

Molecularity	Sample Equation	Rate Law
unimolecular	$A \rightarrow$ product	rate = $k[A]$
bimolecular	$A + A \rightarrow$ product $A + B \rightarrow$ product	rate = $k[A]^2$ rate = $k[A][B]$
termolecular	$A + A + A \rightarrow$ product $A + A + B \rightarrow$ product	rate = $k[A]^3$ rate = $k[A]^2[B]$

16. How is the rate-law determined for a multi-step reaction mechanism with a slow-initial step?____________________

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17. How is determining the rate-law for a multi-step reaction mechanism with a fast-initial step different than for one with a slow-initial step? ____________________

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18. How do catalysts affect reaction rate (& how do they change variables in the Arrhenius equation)? ____________________

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19. Define:
    a. Homogeneous catalyst: ____________________
    b. Heterogeneous catalyst: ____________________
    c. Adsorption: ____________________
    d. Absorption: ____________________

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20. Compare & contrast acid catalysis & base catalysis: ____________________

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21. Describe surface catalysis: ____________________

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22. Describe enzymatic catalysis: ____________________

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Calculations

23. *The data in the table below were obtained for the reaction:*

$$2\,ClO_2\,(aq) + 2\,OH^-\,(aq) \rightarrow ClO_3^-\,(aq) + ClO_2^-\,(aq) + H_2O\,(l)$$

a. What is the order of the reaction with respect to ClO_2?
[ClO_2] triples, rate goes up by 9x, so [ClO_2]^2

b. What is the order of the reaction with respect to OH^-?
[OH] triples, rate goes up by 3x, so [OH]^1

c. What is the overall order of the reaction?
Rate = k[ClO_2]^2[OH]

d. What is the magnitude of the rate constant for the reaction?
k = rate/[ClO_2]^2[OH] = 0.0248/[0.060]^2[0.030] = 230 /M^2s

Experiment Number	[ClO_2] (M)	[OH^-] (M)	Initial Rate (M/s)
1	0.060	0.030	0.0248
2	0.020	0.030	0.00276
3	0.020	0.090	0.00828

24. *The rate law for a reaction is rate = k [A][B]^2:*

a. What is the overall reaction order? ___3rd___

b. How would the rate change if the [A] was tripled? ___Rate would increase by 3x___

c. How would the rate change if the [B] was halved? ___Rate would be reduced by ¼x___

d. How would the rate change if the [A] was doubled and [B] was quartered? ___Rate would be reduced by ⅛x___

25. The following reaction is second order in [A] and the rate constant is 0.025 $M^{-1}s^{-1}$:

$$A \rightarrow B$$

The concentration of A was 0.65 M at 33 s. Find the initial concentration of A.

$1/[A]_t = kt + 1/[A]_0$

$1/[A]_0 = 1/[A]_t - kt$

$1/[A]_0 = 1/[.65] - 0.025\ M^{-1}s^{-1}(33s)$

$1/[A]_0 = 1.54 - 0.825\ M^{-1}$

$1/[A]_0 = 0.71\ M^{-1}$

$\boxed{[A]_0 = 1.4\ M}$

26. A compound decomposes by a first-order process. If 25.0% of the compound decomposes in 60.0 minutes, the half-life of the compound is
$t_{1/2} = \ln 2/k$
but to use the formula, we need to know the value of k. So, using the integrated rate law and the values 0.750 for $[A]_{60.0}$ and 1.000 for $[A]_0$, we can calculate the value of k. (btw - You could also use 75.0 and 100.0 for the concentrations & get the same answer.)

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

$k = (\ln[A]_t - \ln[A]_0)/-t$

$k = (\ln[0.750] - \ln[1.00])/-60.0\text{min} = 4.79 \times 10^{-3}\text{min}^{-1}$

$t_{1/2} = \ln 2/(4.79\times10^{-3}\text{min}^{-1}) = \boxed{145 \text{ minutes}}$

27. For the elementary reaction; $NO_3 + CO \rightarrow NO_2 + CO_2$, the molecularity of the reaction is bimolecular, and the rate law is rate = __$k[NO_3][CO]$________________.

28. A second-order reaction has a half-life of 18 s when the initial concentration of reactant is 0.71 M. The rate constant for this reaction is __________ $M^{-1}s^{-1}$.

$t_{1/2} = 1/k[A]_0$

$k = 1/t_{1/2}[A]_0 = 1/(18\text{s}\bullet0.71M) = \boxed{7.8 \times 10^{-2}\ M^{-1}s^{-1}}$

29. The decomposition of N_2O_5 in solution in carbon tetrachloride proceeds via the reaction

$$2N_2O_5\ (soln) \rightarrow 4NO_2\ (soln) + O_2\ (soln)$$

The reaction is first order and has a rate constant of $4.82 \times 10^{-3}s^{-1}$ at 64°C. If the reaction is initiated with 0.058 mol in a 1.00-L vessel, how many moles remain after 151 s?

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

$\ln[A]_{151} = -4.82\times10^{-3}s^{-1}(151s) + \ln[0.058]_0$

$\ln[A]_{151} = -3.575$

$[A]_{151} = e^{-3.575} = 0.028M$ (0.028M in 1.00L = $\boxed{0.028 \text{ moles}}$

30. The reaction; $2NOBr\ (g) \rightarrow 2\ NO\ (g) + Br_2\ (g)$; is a second-order reaction with a rate constant of 0.80 $M^{-1}s^{-1}$ at 11°C. If the initial concentration of NOBr is 0.0440 M, what is the concentration of NOBr after 7.0 seconds?

$1/[A] = kt + 1/[A]_0$

$1/[A]_{7.0} = 0.80M^{-1}s^{-1}(7.0s) + 1/0.0440 = 28.3M^{-1}$

$1/[A]_{7.0} = 28.3M^{-1}$

$[A]_{7.0} = 1/28.3\ M^{-1} = \boxed{0.0353\ M}$

31. What is the rate of appearance of Br_2 when the rate of disappearance of HBr in the gas phase reaction; $2HBr\ (g) \rightarrow H_2\ (g) + Br_2\ (g)$; is 0.301 Ms^{-1} at 150°C.

$$\frac{0.301\ \cancel{\text{mol HBr}}}{\text{L}\bullet\text{s}} \times \frac{1\text{ mol } Br_2}{2\ \cancel{\text{mol HBr}}} \quad \boxed{= 0.150\text{ mol } Br_2/\text{L}\bullet\text{s}\ \ (0.150M/s)}$$

32. *The peroxydisulfate ion* ($S_2O_8^{2-}$) *reacts with the iodide ion in aqueous solution via the reaction:*

$$S_2O_8^{2-}\ (aq) + 3I^- \rightarrow 2SO_4\ (aq) + I_3^-\ (aq)$$

An aqueous solution containing 0.050 M *of* $S_2O_8^{2-}$ *ion and* 0.072 M *of* I^- *is prepared, and the progress of the reaction followed by measuring* $[I^-]$. *The data obtained is given in the table below.*

Time (s)	0.000	400.0	800.0	1200.0	1600.0
$[I^-]$ (M)	0.072	0.057	0.046	0.037	0.029

a. The average rate of disappearance of I^- in the initial 400.0 s is _(0.072 – 0.057)M / 400.0s = $\boxed{3.8 \times 10^{-5}}$_ M/s.

b. The average rate of disappearance of I^- between 400.0 s and 800.0 s is _(0.057 – 0.046)M / 400.0s = $\boxed{2.8 \times 10^{-5}}$_ M/s.

c. The concentration of $S_2O_8^{2-}$ remaining at 400 s is _0.045_ M.

$$-0.015\ \cancel{\text{mol } I^-} \times \frac{1\text{ mol } S_2O_8^{2-}}{} = -0.0050\ M\ S_2O_8^{2-}$$

$\Delta[I^-]_{0.000\text{-}400.0s} = 0.057 - 0.072 = -0.015M$ L•s 3 ~~mol I~~$^-$

0.050 M $S_2O_8^{2-}$ - 0.0050 M $S_2O_8^{2-}$ = $\boxed{0.045\ M}$