Chapter 14 exercises

Q1. Practice exercise page 576

For the reaction A → B the concentration of (B) after 40 s = 0.70 mole and at 0 s the concentration

of (B) = 0, calculate the average rate of appearance of (B).

Answer:

Average rate = $\Delta[B]$ / Δt = (0.70 mol – 0 mol) / (40 s – 0 s) = 1.8 x 10^{-2} M/s

Q2. Practice exercise page 578

Using the figure 14.4, determine rate instantaneous of C_4H_9Cl at t = 300 s.

Answer:

Rate = - $\Delta[C_4H_9Cl]$ / Δt = - (0.067 – 0.100) / (300 s – 0 s) = 1.1 x 10^{-4} M/s

Q3. Practice exercise page 579

The decomposition of N_2O_5 at a particular instant in a reaction vessel is 4.2 x 10^{-7} M/s, what

is the rate appearance of a) NO_2 , b) O_2 ?

Answer:

a) Rate = - ½ $\Delta[N_2O_5]$ / Δt = ¼ $\Delta[NO_2]$ / Δt = 1/1 $\Delta[O_2]$ / Δt

- $\Delta[NO_2]$ / Δt = 4/2 $\Delta[N_2O_5]$ / Δt = 4/2 x 4.2 10^{-7} M/s

b) - $\Delta[O_2]$ / Δt = ½ $\Delta[N_2O_5]$ / Δt = ½ x 4.2 x10^{-7} = 2.1 x 10^{-7} M/s

Q4. Practice exercise page 583

a) What is the reaction order of the reactant H_2 in $H_{2 (g)}$ + $I_{2 (g)}$ → $2HI_{(g)}$

Rate = k $[H_2]$ $[I_2]$

b) What are the units of the rate constant for the equation?

Answer:

a) The reaction order for H_2 is = 1.

b) over all the reaction order   1 + 1 = 2

Unit of rate constant = (M/s) /(M^2) = $M^{-1}s^{-1}$

Q5. Practice exercise page 587

The following data were measured for the reaction $2NO_{(g)} + 2H_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$

Experiment number	[NO] M	[H₂] M	initial rate (M/s)
1	0.10	0.10	1.23×10^{-3}
2	0.10	0.20	2.46×10^{-3}
3	0.20	0.10	4.92×10^{-3}

    a) Determine the rate law for the reaction.
    b) Calculate the rate constant.
    c) Calculate the rate when [NO] = 0.050 M and [H₂] = 0.15 M.

Answer:

a) Rate 2 / Rate 1 $= k \times (0.1)^m \times (0.2)^n / k \times (0.1)^m \times (0.1)^n = 2.46 \times 10^{-3} / 1.23 \times 10^{-3}$

$$(2/1)^n = 2 \qquad n = 1$$

Rate 3 / Rate 1 $= k \times (0.2)^m \times (0.1)^n / k \times (0.1)^m \times (0.1)^n = 4.92 \times 10^{-3} / 1.23 \times 10^{-3}$
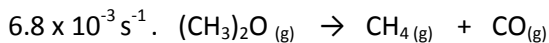
$$2^m = 4 = 2^2 \qquad m = 2$$

Rate law $= k \, [NO]^2 \, [H_2]$

b) $2.46 \times 10^{-3} = k \times (0.1)^2 \times (0.2) = 1.23 \, M^{-2}s^{-}$

c) rate $= 1.23 \times (0.05)^2 \times (0.15) = 4.6 \times 10^{-4}$ M/s

Q6. Practice exercise page 587

Composition of dimethyl ether $(CH_3)_2O$ at 510°C is a first order process with a rate constant of

$6.8 \times 10^{-3} s^{-1}$. $(CH_3)_2O_{(g)} \rightarrow CH_{4(g)} + CO_{(g)}$

If the initial pressure of $(CH_3)_2O$ is 135 torr. What is the pressure after 1420 s?

Answer:

$Ln \, [A]_t = -kt + ln \, [A]_o$

$Ln \, [(CH_3)_2O]_t = -6.8 \times 10^{-4} s^{-1} \times 1420 \, s + ln \, (135)$

$$= -0.9656 + 0.3001 = -0.6655$$

$[CH_3)_2O = 51$ torr

Q7. Practice exercise page 591

a) Calculate t ½ for decomposition of insecticide when k= 1.45 yr^{-1}.

b) How long does it take for concentration of the insecticide to reach one quarter of initial value?

Answer:

a) $t_{1/2}$ = 0.693 / 1.45 yr^{-1} = 0.478 yr

b) one quarter = ¼ = ½ x ½ which is 2 x (1/2)

   0.478 yr x 2 = 0.956 yr

Q8. Practice exercise page 597

Calculate the rate constant for the rearrangement of methyl iso nitrile at 280˚C. E_a = 160 KJ/mol and rate constant at 462.9 ˚K = 2.52 x 10^{-5}.

Answer:

Ln (k_1/ 2.52 x 10^{-5}) = (160 KJ/mol)/ 8.314 J/mol-K) (1/462.9 – 1/553)x (1000J/1KJ)

= 6.774

K_1/ 2.52 x 10^{-5} = $e^{6.774}$ = 874.91

K_1 = 2.2 x $10^{-2} s^{-1}$.

Q9. Practice exercise page 595

Imagine you have three reactions with, E_a = 40, 25, and 15 KJ/mol, respectively. Rank the reactions from slowest to faster.
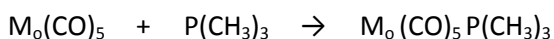
Answer:

The lower the activation energy , the faster the reaction

(2) < (1) < (3)

Q10. Practice exercise 19 page 599

For the reaction $M_o (CO)_6$ + $P(CH_3)_3$ → $M_o (CO)_5 P(CH_3)_3$ + CO the proposed mechanism is:

$M_o(CO)_6$ → $M_o (CO)_5$ + CO

$M_o(CO)_5$ + $P(CH_3)_3$ → $M_o (CO)_5 P(CH_3)_3$

a) Is the proposed mechanism consistent with the equation for the overall reaction?

b) What is the molecularity of each step of the mechanism?

c) Identify the intermediates.

Answer:

 a) yes the two equations added to yield the equation of the reaction.

b) The first reaction is unimolecular and the second step is bimolecular.

c) The intermediate is $M_o(CO)_5$.

Q11. Practice exercise 600

Consider the following reaction $2NO_{(g)} + Br_{2\,(g)} \rightarrow 2NOBr_{(g)}$

a) write the rate law for the reaction, assuming it involves a single elementary reaction.

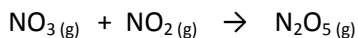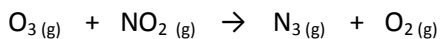b) Is a single step mechanism likely for this reaction.

Answer:

a)   Rate $= k\,[NO_g]^2\,[Br_g]$

b) No, because termolecular reactions are very rare.

Q12. Practice exercise page 602

 Ozone reacts with nitrogen dioxide to produce dinitrogen pentaoxide and oxygen.

$O_{3\,(g)} + 2NO_{2\,(g)} \rightarrow N_2O_{5\,(g)} + O_{2\,(g)}$
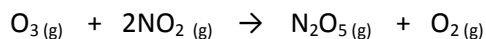
 The reaction is believed to occur two steps.

$O_{3\,(g)} + NO_{2\,(g)} \rightarrow N_{3\,(g)} + O_{2\,(g)}$

$NO_{3\,(g)} + NO_{2\,(g)} \rightarrow N_2O_{5\,(g)}$

 The experimental rate law is   rate $= k\,[O_3]\,[NO_2]$. What can you say about the relative rates

of the two steps of the mechanism?

Answer:

 Because the rate law conforms to the molecularity of the first step, that must be the rate

determining step. The second step must be much faster than the first one.

Exercises page 616

14.15

Consider the following aqueous reaction, $A_{aq} \rightarrow B_{aq}$. A flask is charged with 0.065 mole of (A)

in total volume of 100.0 mL. The following data are collected.

Time (min)	0	10	20	30	40
Mole of (A)	0.065	0.051	0.042	0.036	0.031

a) Calculate the number of moles of (B) at each time in the table, assuming that there no

   molecules of (B) at time zero.

b) Calculate the average rate of disappearance of (A) for each 10 min interval in unit M/s.

c) Between t = 0 min and t = 30 m9n, what is the average rate of appearance of (B) in unit M/s?
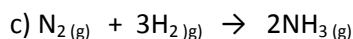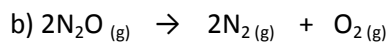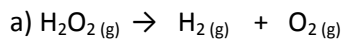
   Assume that the volume of the solution is constant.

Answer: a) and b)

Time (min)	mole A	mole B	[A] mol/L	Δ[A]	R M/s
0	0.065	0	0.65		
10	0.051	0.01`4	0.51	- 0.14	2.3×10^{-3}
20	0.042	0.023	0.42	- 0.09	1.5×10^{-3}
30	0.036	0.030	0.36	- 0.06	1.0×1^{-3}
40	0.031	0.034	0.31	- 0.05	0.8×10^{-3}

b) Rate = Δ[B] / Δt = (0.36 – 0.51) / (30 – 10) = 1.3 x 10+-4 M/s

14.19

For each of the following gas-phase reactions, indicate how the rate of disappearance of each

reactant is related to the appearance of each product.

a) $H_2O_{2(g)} \rightarrow H_{2(g)} + O_{2(g)}$

b) $2N_2O_{(g)} \rightarrow 2N_{2(g)} + O_{2(g)}$

c) $N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

Answer:

    a) $- \Delta[H_2O] / \Delta t$ $= \Delta[H_2] / \Delta t$ $= \Delta[O_2] / \Delta t$

    b) $- \frac{1}{2} \Delta[N_2O] / \Delta t$ $= \frac{1}{2} \Delta[N_2] / \Delta t$ $= \Delta[O_2] / \Delta t$

    c) $- \Delta[N_2] / \Delta t$ $= - 1/3 \Delta[H_2] / \Delta t$ $= \frac{1}{2} \Delta[NH_3] / \Delta t$

14.21

   a) Consider the combustion of H_2 gas ($2H_{2\,(g)} + O_{2\,(g)} \rightarrow 2H_2O_{(g)}$). If H_2 is burned at a rate of

   0.85 mol / s. What is the rate of consumption of O_2? What is the rate of formation of water

   Vapor?

   b) the reaction $2NO_{(g)} + Cl_{2\,(g)} \rightarrow 2NOCl_{(g)}$ is carried out in close vessel. If the partial pressure of

   NO is decreasing at the rate of 23 torr / min, what is the rate of change of total pressure of the

   vessel.

Answer:

    a)   Rate of H_2 = 0.85 mol / s

      $- \frac{1}{2} \Delta H_2] / \Delta t$ $= - \Delta[O_2] / \Delta t = \frac{1}{2} \Delta[H_2O] / \Delta t$

      -    $\frac{1}{2} \times 0.85 = - \Delta[O_2] / \Delta t = 0.425$ mol / s

    $\frac{1}{2} \Delta[H_2O] / \Delta t = - \frac{1}{2} \Delta[H_2] / \Delta t = 0.85$ mol/s

   b) $- \frac{1}{2} \Delta[NO] / \Delta t = \Delta[Cl] / \Delta t$

     $\frac{1}{2} \times 23 = \Delta[Cl] / \Delta t = 11.5$ torr   (11.5 torr + 23 torr = 34.5 torr/min for the reactants)

     $- \frac{1}{2} \Delta[NO] / \Delta t = \frac{1}{2} \Delta[NOCl] / \Delta t$

     $\Delta[NOCl] / \Delta t = 23$ torr/min

     rate change = reactants – products = 35.5 – 23 = 11.5 = 12 torr/min

14.23

   A reaction n A + B $\rightarrow$ C obeys the following rate law Rate = $k\,[B]^2$

a) If [A] doubled. How will the rate change? Will the rate constant?

b) what are the reaction order for A and B? what is the overall reaction order?

c) What are the units of the rate constant?

Answer:

a) If [A] doubled, there is no change in the rate or the rate constant. Because [A] does not

   Apper in the rate law $= k[B]^2$.

b) the reaction is zero order in A, second order in B, and second order overall.

c) unit $k = M^{-1}s^{-1}$

14.25

The decomposition of N_2O_5 in CCl_4 proceeds as follows: $2N_2O_5 \rightarrow 4NO_2 + O_2$. The rate law is

first order in N_2O_5. At 64°C the rate constant is $4.82 \times 10^{-3}s^{-1}$.

a) write the rate law for the reaction.

b) What is the rate of reaction when $[N_2O_5] = 0.024$ M?

c)What happens to the rate when the concentration of N_2O_5 is doubled to 0.0480 M?

Answer:

a) rate $= k [N_2O_5]$

b) rate $= 4.82 \times 10^{-3}s^{-1} \times 0.024$ M $= 1.157 \times 10^{-4}$ m/s $= 1.16 \times 10^{-4}$ M/s

c) rate $= 4.82 \times 10^{-3}s^{-1} \times 0.048 = 2.32 \times 10^{-4}$

14.29

The iodide ion reacts with hypochlorite ion in the following way: $OCl^- + I^- \rightarrow OI^- + Cl^-$.

This rapid reaction gives the following rate data

[OCl⁻] M	[I⁻] M	rate M/s
1.5×10^{-3}	1.5×10^{-3}	1.36×10^{-4}
3.0×10^{-3}	1.5×10^{-3}	1.72×10^{-4}
1.5×10^{-3}	3.0×10^{-3}	2.72×10^{-4}

a) Write the rate law for this reaction.

b) Calculate the rate constant.

c) Calculate the rate when $[OCl^-] = 2.0 \times 10^{-3}$ and $[I^-] = 5.0 \times 10^{-4}$ M.

Answer:

a) Rate 2 / Rate 1 $= [k (3.0 \times 10^{-3})^m (1.5 \times 10^{-3})^n] / [k (1.5 \times 10^{-3})^m (1.5 \times 10^{-3})^n]$

$= (2.72 \times 10^{-4}) / (1.36 \times 10^{-4}) = 2$

$2^m = 2^1 \quad m = 1$

Rate 3 / Rate 1 $= [k (1.5 \times 10^{-3})^m (3.0 \times 10^{-3})^n] / [k (1.5 \times 10^{-3})^m (1.5 \times 10^{-3})^n]$

$= (2.72 \times 10^{-4}) / (1.36 \times 10^{-4}) = 2$

$2^2 = 2^1 \quad n = 1$

b) 1.36×10^{-4} M/s $= k (1.5 \times 10^{-3}$ M$)(1.5 \times 10^{-3}$ M$)$

k = 60 M/s

c) rate = 60 $M^{-1}s^{-1} \times (2.0 \times 10^{-3}$ M$)(5.0 \times 10^{-4}$ M$) = 6/0 \times 10^{-5}$ M/s

14.37

a) The gas phase decomposition of SO_2Cl_2 ($SO_2Cl_{2\,(g)} \rightarrow SO_{2\,(g)} + Cl_{2\,(g)}$) is first in SO_2Cl_2. At 600 k the

half-life for this process is 2.3×10^5 s. What is the rate constant at this temperature?

b)At 320°C the rate constant is $2.2 \times 10^{-5}\,s^{-1}$. What is the half-life at this temperature?

Answer:

a) k $= 0.693 / t_{1/2} = 0.693 / 2.3 \times 10^5$ s $= 3.0 \times 10^{-6}\,s^{-1}$

b) $t_{1/2} = 0.693 / 2.2 \times 10^4$ s

14.41

The reaction $SO_2Cl_{2\,(g)} \rightarrow SO_{2\,(g)} + Cl_{2\,(g)}$ is the first order in SO_2Cl_2. Using the following kinetic data, determine the magnitude of the first order rate constant.

time (s)	0	2,500	5,000	7,500	10,000
pressure SO_2Cl_2 (atm)	1.000	0.947	0.895	0.848	0.803

Answer:

Slope $=$ (ln 0.803 - ln 0.895) / (10,000 – 5,000) $=$ (-0.2194 – (- 0.1109))/ 5000 $= 2.17 \times 10^5$ s

14.49

Calculate the fraction of atoms in a sample of argon gas at 400°C that has an energy of 10.0 KJ or greater.

Answer:

$-E_a / RT$ $=$ $- (10.0 \times 1000$ J$) / (8.314$ J/mol-K$)(400$ K$) = - 3.007$

$f = e^{-3.007} = 0.0494 = 4.94 \times 10^{-2}$

14.53

Based on their activation energies and energy changes as assuming that all collision are the same, which of the following reactions would be fastest and which would be lowest? explain your answer.

A) $E_a = 45$ KJ/mol, $\Delta E = - 25$ KJ/mol

b) $E_a = 35$ KJ/mol, $\Delta E = - 10$ KJ/mol

c) $E_a = 55$ KJ/mol, $\Delta E = 10$ KJ/mol

Answer:

The lowest the activation energy, the faster the reaction

(b) faster than (a) faster than (c)

b $>$ a $>$ c

14.55

A certain first order reaction has a rate constant of $2.75 \times 10^{-2} s^{-1}$ at 20°C. What is the valu

of (k) at 60°C if a) $E_a = 75.5$ KJ/mol and b) $E_a = 125$ KJ/mol.

Answer:

a) $\ln k_1 / \ln k_2 = E_a /R (1/T_2 - 1/T_1)$

$\ln k_1 / (2.75 \times 10^{-2}) = (75.5 \times 1000 / 8.314) \times (1/293 - 1/333) = 3.723$

$k_1 / 2.75 \times 10^{-2} = e^{3.723} = 41.397$

$k_1 = 1.14 s^{-1}$

b) $\ln k_1 / (2.75 \times 10^{-2}) = (125 \times 1000 / 8.314) \times (1/293 - 1/333)$

$k_1 = 13 s^{-1}$

14.59

The activation energy of a certain is 65.7 KJ/mol. How many times faster will the reaction occur

at 50°C than 0°C?

Answer:

$f = e^{-Ea / RT}$

- Ea / RT = - (65.7 x 1000 J/mol) / (8.314 J/mol-K)(273 K) = - 28.946

$f = e^{-28.946} = 2.684 \times 10^{-13}$

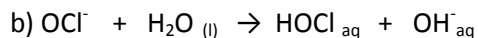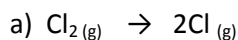- Ea / RT = - (65.7 x 1000 J/mol) / (8.314 J/mol-K)(323 K) = - 24.465
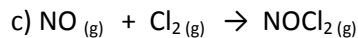
$f = e^{-24.465} = 2.37 \times 10^{-11}$

$(2.37 \times 10^{-11}) / (2.684 \times 10^{-13}) = 0.883 \times 10^{2} = 88$

The reaction will occur 88 time faster at 50°C, assuming equal initial concentrations.

14.63

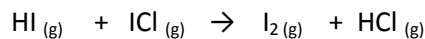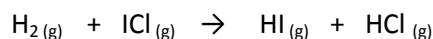What is molecularity of each of the following elementary reaction? Write the law for each.

a) $Cl_{2 (g)} \rightarrow 2Cl_{(g)}$

b) $OCl^- + H_2O_{(l)} \rightarrow HOCl_{aq} + OH^-_{aq}$

c) NO $_{(g)}$ + Cl$_2$ $_{(g)}$ → NOCl$_2$ $_{(g)}$

Answer:

    a) unimolecular   R = k [Cl$_2$]

    b) bimolecular   R = k [OCl$^-$] [H$_2$O]

    c) bimolecular R = k [NO] [Cl$_2$]

14.67

The following mechanism has been proposed for the gas-phase reaction of H$_2$ with ICl.

H$_2$ $_{(g)}$ + ICl $_{(g)}$ → HI $_{(g)}$ + HCl $_{(g)}$

HI $_{(g)}$ + ICl $_{(g)}$ → I$_2$ $_{(g)}$ + HCl $_{(g)}$

a) Write the balance equation for the overall reaction.

b) Identify any intermediate in the mechanism.

c) Write rate laws for each elementary reaction in the mechanism.

d) If the first step is slow and the second one is fast, what rate law do you expect to be observed

    for the overall reaction?

Answer:

    a) H$_2$ $_{(g)}$ + 2ICl $_{(g)}$ → I$_2$ $_{(g)}$ + 2HCl $_{(g)}$

    b) HI is the intermediate.

    c) first step : rate = k$_1$ [H$_2$] [ICl] ,   second step : rate = k$_2$ [HI] [ICl]

    d) If the first step is slow, the rate is = k [H$_2$] [ICl].

14.81

The activation energy of uncatalyzed reaction is 95 KJ/mol. The addition of a catalyst lowers the

Activation energy to 55 KJ/mol. Assuming that the collision factor remains the same, by what factor

Will the catalyst increase the rate of the reaction a) 25°C and b) 125°C?

Answer:

    a)   at 25°C

    $k_1 = A\ e^{-Ea/RT}$ $-Ea/RT = (-95000\ J/mol) / (8.314\ Jlmol\text{-}K)\ (298\ K) = -38.344$

    $k_1 = A\ e^{-38.344} = A \times 2.225 \times 10^{-17}$

    $k_2 = A\ e^{-Ea/RT}$ $-Ea/RT = (-55000\ J/mol) / (8.314\ J/mol\text{-}K)\ (298\ K) = -22.199$

    $k_2 = A\ e^{-22.199} = A \times 2.286 \times 10^{-10}$

    $k_2 / k_1 = (A \times 2.286 \times 10^{-10}) / (A \times 2.225 \times 10^{-17}) = 1.03 \times 10^{7}$

    The analyzed reaction is approximately 10,000,000 times faster at 25°C.

    b) at 125°C

    $k_1 = A\ e^{-Ea/RT}$ $-Ea/RT = (-95000\ J) / (8.314\ J/mol\text{-}K)\ (398\ K) = -28.71$

    $k_1 = A\ e^{-28.71} = A \times 3.4 \times 10^{-13}$

    $k_2 = A\ e^{-Ea/RT}$ $-Ea/RT = (-55000\ J) / (8.314\ J/mol\text{-}K)\ (398\ K) = -16.6215$

    $k_2 = A\ e^{-16.6215} = A \times 6.045 \times 10^{-8}$

    $k_2 / k_1 = (A \times 6.045 \times 10^{-8}) / (A \times 3.4 \times 10^{-13}) = 1.8 \times 10^{5}$

    The catalyst reaction is 180,000 time faster at 125°C.

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