Section 78 – Rate Laws

78-1. How do the rate of a reaction and its rate constant differ?

Solution

A rate of reaction is a change in concentration per unit time; the rate of a reaction is proportional to its rate constant, and it typically increases with concentration of reactants. A rate constant is a characteristic property of a reaction that indicates its intrinsic speed; a large rate constant is characteristic of a rapid reaction. The rate constant for a given reaction does not change (it is *constant*) unless the temperature changes.

78-2. Doubling the concentration of a reactant increases the rate of a reaction four times. With this knowledge, answer the following questions:

(a) What is the order of the reaction with respect to that reactant?

(b) Tripling the concentration of a different reactant increases the rate of a reaction three times. What is the order of the reaction with respect to that reactant?

Solution

(a) Since the concentration of the reactant doubled and the rate quadrupled, we can conclude that the order with respect to the reactant is 2, since $2^2 = 4$.

$$\text{rate} = k[\text{reactant}]^m$$

$$4(\text{rate}) = k[2(\text{reactant})]^2;$$

(b) Since the concentration of the reactant and the rate both tripled, we can conclude that $m = 1$, and the order with respect to this reactant is 1.

$$\text{rate} = k[\text{reactant}]^m$$

$$3(\text{rate}) = k[3(\text{reactant})]^1$$

78-3. Tripling the concentration of a reactant increases the rate of a reaction nine-fold. With this knowledge, answer the following questions:

(a) What is the order of the reaction with respect to that reactant?

(b) Increasing the concentration of a reactant by a factor of four increases the rate of a reaction four-fold. What is the order of the reaction with respect to that reactant?

Solution

(a) Since the concentration of the reactant tripled and the rate increased nine fold, we can conclude that the order with respect to the reactant is 2, since $3^2 = 9$.

$$\text{rate} = k[\text{reactant}]^m$$
$$9(\text{rate}) = k[3(\text{reactant})]^2;$$

(b) Since the concentration of the reactant and the rate both quadrupled, we can conclude that $m = 1$, and the order with respect to this reactant is 1.

$$\text{rate} = k[\text{reactant}]^m$$
$$4(\text{rate}) = k[4(\text{reactant})]^1$$

78-4. How will the rate of reaction change for the process:

$CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$ if the rate law for the reaction is $\text{rate} = k[NO_2]^2$?

(a) Decreasing the pressure of NO_2 from 0.50 atm to 0.250 atm.
(b) Increasing the concentration of CO from 0.01 *M* to 0.03 *M*.

Solution

(a) $$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[0.25\ NO_2]^2}{k[0.50\ NO_2]^2} = \frac{0.0625}{0.25} = \frac{1}{4}$$

Since rate_1 is four times as large as rate_2, the process reduces the rate by a factor of 4. (b) Since CO does not appear in the rate law, the rate is not affected.

78-5. How will each of the following affect the rate of the reaction:

$CO(g) + NO_2(g) \longrightarrow CO_2(g) + NO(g)$ if the rate law for the reaction is $\text{rate} = k[NO_2][CO]$?

(a) Increasing the pressure of NO_2 from 0.1 atm to 0.3 atm
(b) Increasing the concentration of CO from 0.02 *M* to 0.06 *M*

Solution

(a) $$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k[0.3\,\text{atm}][CO]}{k[0.1\,\text{atm}][CO]} = 3$$

The rate increases by a factor of 3.
(b) Concentration increases by a factor of 3; the rate increases by a factor of 3.

78-6. Regular flights of supersonic aircraft in the stratosphere are of concern because such aircraft produce nitric oxide, NO, as a byproduct in the exhaust of their engines. Nitric oxide reacts with ozone, and it has been suggested that this could contribute to depletion of the ozone layer. The reaction $NO + O_3 \longrightarrow NO_2 + O_2$ is first order with respect to both NO and O_3 with a rate constant of 2.20×10^7 L/mol/s. What is the instantaneous rate of disappearance of NO when $[NO] = 3.3 \times 10^{-6}$ *M* and $[O_3] = 5.9 \times 10^{-7}$ *M*?

Solution

Rate = $k[NO][O_3] = 2.20 \times 10^7$ L/mol/s$[3.3 \times 10^{-6}\ M][5.9 \times 10^{-7}\ M] = 4.3 \times 10^{-5}$ mol/L/s

78-7. Radioactive phosphorus is used in the study of biochemical reaction mechanisms because phosphorus atoms are components of many biochemical molecules. The location of the phosphorus (and the location of the molecule it is bound in) can be detected from the electrons (beta particles) it produces:

$${}^{32}_{15}P \longrightarrow {}^{32}_{16}S + e^-$$

rate = 4.85×10^{-2} day$^{-1}\left[{}^{32}P\right]$

What is the instantaneous rate of production of electrons in a sample with a phosphorus concentration of 0.0033 *M*?

Solution

Rate = 4.85×10^{-2} day$^{-1}[0.0033\ M] = 1.6 \times 10^{-4}$ mol/L/d

78-8. The rate constant for the radioactive decay of ^{14}C is 1.21×10^{-4} year^{-1}. The products of the decay are nitrogen atoms and electrons (beta particles):

$${}^{14}_{6}C \longrightarrow {}^{14}_{6}N + e^-$$

rate = $k\left[{}^{14}_{6}C\right]$

What is the instantaneous rate of production of N atoms in a sample with a carbon–14 content of $6.5 \times 10^{-9}\ M$?

Solution

rate = 1.21×10^{-4} year^{-1} $[6.5 \times 10^{-9}\ M] = 7.9 \times 10^{-13}$ mol/L/year

78-9. The decomposition of acetaldehyde is a second order reaction with a rate constant of 4.71×10^{-8} L mol^{-1} s^{-1}. What is the instantaneous rate of decomposition of acetaldehyde in a solution with a concentration of $5.55 \times 10^{-4}\ M$?

Solution

rate = $k[\text{acetaldehyde}]^2 = 4.71 \times 10^{-7}$ L/mol/s $[5.55 \times 10^{-4}$ mol/L$]^2 = 1.45 \times 10^{-13}$ mol/L/s

CORRECTION by DV:

rate = $k[\text{acetaldehyde}]^2 = 4.71 \times 10^{-8}$ L/mol/s $[5.55 \times 10^{-4}$ mol/L$]^2 = 1.45 \times 10^{-14}$ mol/L/s

78-10. Alcohol is removed from the bloodstream by a series of metabolic reactions. The first reaction produces acetaldehyde; then other products are formed. The following data have been determined for the rate at which alcohol is removed from the blood of an average male, although individual rates can vary by 25–30%. Women metabolize alcohol a little more slowly than men:

$[C_2H_5OH]$ (*M*)	4.4×10^{-2}	3.3×10^{-2}	2.2×10^{-2}

Rate (mol L^{-1} h^{-1})	2.0×10^{-2}	2.0×10^{-2}	2.0×10^{-2}

Determine the rate law, the rate constant, and the overall order for this reaction.

Solution

The rate is independent of the concentration. Therefore, rate = k; $k = 2.0 \times 10^{-2}$ mol L^{-1} h^{-1} (about 0.9 g L^{-1} $h^{-1}$for the average male); The reaction is zero order—that is, it does not depend on the concentration of any reagent.

78-11. Under certain conditions the decomposition of ammonia on a metal surface gives the following data:

$[NH_3]$ (M)	1.0×10^{-3}	2.0×10^{-3}	3.0×10^{-3}
Rate (mol L^{-1} h^{-1})	1.5×10^{-6}	1.5×10^{-6}	1.5×10^{-6}

Determine the rate law, the rate constant, and the overall order for this reaction.

Solution

The rate does not change as the concentration changes. The reaction is zero order because it is independent of the concentration: rate = k; $k = 1.5 \times 10^{-6}$

78-12. Nitrosyl chloride, NOCl, decomposes to NO and Cl_2.

$$2NOCl(g) \longrightarrow 2NO(g) + Cl_2(g)$$

Determine the rate law, the rate constant, and the overall order for this reaction from the following data:

[NOCl] (M)	0.10	0.20	0.30
Rate (mol L^{-1} h^{-1})	8.0×10^{-10}	3.2×10^{-9}	7.2×10^{-9}

Solution

The object of this problem is to use the general rate expression: rate = $k[NOCl]^m$, first to determine the value of m and then, by substituting data from one experiment into the equation, to find the value of k. The data listed as substituted into the rate law give:
Experiment 1: 8.0×10^{-10} mol/L/h = $k[0.10 \text{ mol/L}]^m$
Experiment 2: 3.20×10^{-9} mol/L/h = $k[0.20 \text{ mol/L}]^m$
Experiment 3: 7.2×10^{-9} mol/L/h = $k[0.30 \text{ mol/L}]^m$
The value of m can be found by inspection. Examining Experiments 1 and 2, it is found that the rate increases by a factor of four as the concentration increases by a factor of two; from Experiments 1 and 3, the rate increases by a factor of nine while the concentration increases by a factor of three. This can happen only if m is 2. The value of k as calculated from the first set of data is:

$$k = \frac{8.0 \times 10^{-10} \text{ mol L}^{-1} \text{ h}^{-1}}{[0.10 \text{ mol L}^{-1}]^2} = 8.0 \times 10^{-8} \text{ L mol}^{-1} \text{ h}^{-1}$$

rate = $k[NOCl]^2$; $k = 8.0 \times 10^{-8}$ L/mol/h; second order

78-13. From the following data, determine the rate law, the rate constant, and the order with respect to A for the reaction $A \longrightarrow 2C$.

[A] (M)	1.33×10^{-2}	2.66×10^{-2}	3.99×10^{-2}
Rate (mol L^{-1} h^{-1})	3.80×10^{-7}	1.52×10^{-6}	3.42×10^{-6}

Solution

Use the general rate expression, rate = $k[A]^m$, first to determine the value of m and then, by substituting data from one experiment into the equation, to find the value of k. The data listed are substituted into three rate laws, all of which apply to the same system:

Experiment 1: 3.80×10^{-7} mol/L/h = $k[1.33 \times 10^{-2}]^m$
Experiment 2: 1.52×10^{-6} mol/L/h = $k[2.66 \times 10^{-2}]^m$
Experiment 3: 3.42×10^{-6} mol/L/h = $k[3.99 \times 10^{-2}]^m$

Find the value of m by inspection. From Experiments 1 and 2, the rate increases by a factor of four as the concentration doubles. Comparing Experiments 1 and 3, the rate increases by a factor of nine as the concentration increases by a factor of three. This situation can occur only if the value of m is 2. The rate law is $\text{Rate} = k[A]^2$ and the reaction is second order. The value of k as calculated from the first set of data is:

$$k = \frac{3.80 \times 10^{-7}\ \text{mol L}^{-1}\ \text{h}^{-1}}{[1.33 \times 10^{-2}\ \text{mol L}^{-1}]^2} = 2.15 \times 10^{-3}\ \text{mol L}^{-1}\ \text{h}^{-1}$$

78-14. Nitrogen monoxide reacts with chlorine according to the equation:

$$2\text{NO}(g) + \text{Cl}_2(g) \longrightarrow 2\text{NOCl}(g)$$

The following initial rates of reaction have been observed for certain reactant concentrations:

[NO] (mol/L)	[Cl_2] (mol/L)	Rate (mol L^{-1} h^{-1})
0.50	0.50	1.14
1.00	0.50	4.56
1.00	1.00	9.12

What is the rate law that describes the rate's dependence on the concentrations of NO and Cl_2? What is the rate constant? What are the orders with respect to each reactant?

Solution

The rate law has the general form:

$$\text{rate} = k[\text{NO}]^m[\text{Cl}_2]^n$$

Comparing the data in rows 1 and 2, [Cl_2] remains constant, [NO] doubles, and the rate becomes four times as large, so $m = 2$. Comparing data in rows 2 and 3, [NP] remains constant, [Cl_2] doubles, and the rate doubles, so $n = 1$. The rate law is:

$$\text{rate} = k[\text{NO}]^2[\text{Cl}_2]$$

Data from row 1 are used to determine k.

$$k = \frac{\text{rate}}{[\text{NO}]^2[\text{Cl}_2]} = \frac{1.14\ \text{mol L}^{-1}\ \text{h}^{-1}}{(0.50\ \text{mol L}^{-1})^2(0.50\ \text{mol L}^{-1})} = 9.1\ \text{L}^2\ \text{mol}^{-2}\ \text{h}^{-1}$$

rate $= k[\text{NO}]^2[\text{Cl}_2]$; second order in NO; first order in Cl_2]

78-15. Hydrogen reacts with nitrogen monoxide to form dinitrogen monoxide (laughing gas) according to the equation: $H_2(g) + 2NO(g) \longrightarrow N_2O(g) + H_2O(g)$

Determine the rate law, the rate constant, and the orders with respect to each reactant from the following data:

[NO] (*M*)	0.30	0.60	0.60
[H_2] (*M*)	0.35	0.35	0.70
Rate (mol L^{-1} s^{-1})	2.835×10^{-3}	1.134×10^{-2}	2.268×10^{-2}

Solution

Use the algebraic method to determine the rate law expression:

$$\frac{\text{rate 2}}{\text{rate 1}} = \frac{0.01134}{0.002835} = \frac{k(0.60)^m(0.35)^n}{k(0.30)^m(0.35)^n}$$

$4.00 = 2.0^m$, $m = 2$

$$\frac{\text{rate 3}}{\text{rate 2}} = \frac{0.02268}{0.01134} = \frac{k(0.60)^m(0.70)^n}{k(0.60)^m(0.35)^n}$$

$2.00 = 2^n$, $n = 1$

To determine the value of the rate constant, data from any one of the three experiments could be substituted into the rate law to solve for *k*. Using data from Experiment 1 gives:

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

$$2.835 \times 10^{-3}\,\text{mol/L/s} = k[0.30\,M]^2[0.35\,M]$$

$$k = \frac{2.835 \times 10^{-3}\ \text{mol L}^{-1}\ \text{s}^{-1}}{[0.30\ m]^2[0.35\ M]} = 9.0 \times 10^{-2}\ \text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$$

78-16. For the reaction $A \longrightarrow B + C$, the following data were obtained at 30 °C:

[*A*] (*M*)	0.230	0.356	0.557
Rate (mol L^{-1} s^{-1})	4.17×10^{-4}	9.99×10^{-4}	2.44×10^{-3}

(a) What is the order of the reaction with respect to [*A*], and what is the rate law?

(b) What is the rate constant?

Solution

(a) The rate law will be of the form rate = $k[A]^m$ and *m* will be the same for all three sets of experimental data. Therefore, we can write:

Experiment 1: 4.17×10^{-4} mol/L/s = $k[0.230\ M]^m$

Experiment 2: 9.99×10^{-4} mol/L/s = $k[0.356\ M]^m$

Experiment 3: 2.44×10^{-3} mol/L/s = $k[0.557\ M]^m$

The first two experiments can be set up so as to cancel one of the unknowns (that is, k) and solve for the other unknown (that is, m):

$$\frac{4.17 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}}{9.99 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}} = \frac{(0.230\ M)^m}{(0.356\ M)^m}$$

$$0.4174 = \frac{(0.230\ M)^m}{(0.356\ M)^m}$$

Taking the natural log of each side gives:

$\ln 0.4174 = m(\ln 0.230) - m(\ln 0.356)$

$-0.8737 = -1.4697m + 1.0328m$

$-0.8737 = -0.4369m$

$$m = \frac{-0.8737}{-0.4369} = 2.00$$

Therefore, the rate law is second order in A and is written as rate = $k[A]^2$. (b) The rate constant can be calculated from any of the three sets of data by using the rate law in conjunction with data found by substituting any of the three sets of data into the rate law. Using the data from Equation 1 gives:

4.17×10^{-4} mol/L/s = $k[0.230\ M]^2$

$$k = \frac{4.17 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}}{(0.059\ \text{mol}^2\ \text{L}^{-2})} = 7.88 \times 10^{-3}\ \text{L mol}^{-1}\ \text{s}^{-1}$$

78-17. For the reaction $Q \longrightarrow W + X$, the following data were obtained at 30 °C:

$[Q]_{\text{initial}}$ (M)	0.170	0.212	0.357
Rate (mol L^{-1} s^{-1})	6.68×10^{-3}	1.04×10^{-2}	2.94×10^{-2}

(a) What is the order of the reaction with respect to [Q], and what is the rate law?

(b) What is the rate constant?

Solution

(a) Write the rate law using the first two sets of data:

$6.68 \times 10^{-3} = k[0.170]^n$

$1.04 \times 10^{-2} = k[0.212]^n$

Eliminate k:

$$6.68 \times 10^{-3} = \frac{1.04 \times 10^{-2}}{[0.212]^n}[0.170]^n$$

$0.6423 = [0.8019]^n$

$\ln 0.6423 = n(\ln 0.8019)$

$-0.4427 = n(-0.2208)$

$n = 2$;

(b) Using the first set of data and $n = 2$, 6.68×10^{-3} mol/L/s = $k[0.170\ \text{mol/L}]^2$; $k = 0.231$ L/mol/s

78-18. The rate constant for the first–order decomposition at 45 °C of dinitrogen pentoxide, N_2O_5, dissolved in chloroform, $CHCl_3$, is 6.2×10^{-4} min^{-1}.

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

What is the rate of the reaction when $[N_2O_5] = 0.40$ *M*?

Solution

(a) The rate of reaction for a first-order reaction in N_2O_5 is written as rate = $k[N_2O_5]$ where *k*, the rate constant at 45 °C, is 6.2×10^{-4} min^{-1}. When $[N_2O_5] = 0.40$ *M*,

rate = 6.2×10^{-4} min^{-1} (0.40 mol/L) = 2.5×10^{-4} mol/L/min

30. The annual production of HNO_3 in 2013 was 60 million metric tons Most of that was prepared by the following sequence of reactions, each run in a separate reaction vessel.

(a) $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

(b) $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

(c) $3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$

The first reaction is run by burning ammonia in air over a platinum catalyst. This reaction is fast. The reaction in equation (c) is also fast. The second reaction limits the rate at which nitric acid can be prepared from ammonia. If equation (b) is second order in NO and first order in O_2, what is the rate of formation of NO_2 when the oxygen concentration is 0.50 *M* and the nitric oxide concentration is 0.75 *M*? The rate constant for the reaction is 5.8×10^{-6} L^2 mol^{-2} s^{-1}.

Solution

The rate law governing the formation of HNO_3 is:

$$\text{rate} = k[\text{NO}]^2[\text{O}_2]$$

From the data given:

rate = $k[0.75 \text{ mol L}^{-1}]^2[0.50 \text{ mol/L}]$

= $(5.8 \times 10^{-6} \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1})(0.75 \text{ mol L}^{-1})^2(0.50 \text{ mol/L})$

= 1.631×10^{-6} mol/L/s

= 1.6×10^{-6} mol/L/s

78-19. The following data have been determined for the reaction:

$I^- + OCl^- \longrightarrow IO^- + Cl^-$

	1	2	3
$[I^-]_{initial}$ (M)	0.10	0.20	0.30
$[OCl^-]_{initial}$ (M)	0.050	0.050	0.010
Rate (mol L^{-1} s^{-1})	3.05×10^{-4}	6.20×10^{-4}	1.83×10^{-4}

Determine the rate law and the rate constant for this reaction.

Solution

The rate law has the form rate = $k[I^-]^m[OCl^-]^n$ and the values for m and n must be determined. Comparing data from columns 1 and 2, $[OCl^-]$ remains constant and $[I^-]$ doubles. As $[I^-]$ doubles, the rate doubles, so $m = 1$.

Comparing data from columns 1 and 3,

$3.05 \times 10^{-4} = k[0.10]^1[0.05]^n \longrightarrow 3.05 \times 10^{-3} = k[0.05]^n$

$1.83 \times 10^{-4} = k[0.30]^1[0.01]^n \longrightarrow 6.1 \times 10^{-4} = k[0.01]^n$

The first numerical value is five times larger than the second, corresponding to a fivefold increase in concentration. Therefore, $n = 1$; rate = $k[I^-][OCl^-]$

The rate constant is determined by putting the data from column 2 into the rate law:

$$k = \frac{\text{rate}}{[I^-][OCl^-]} = \frac{6.10 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}}{(0.20\ \text{mol L}^{-1})(0.050\ \text{mol L}^{-1})} = 6.1 \times 10^{-2}\ \text{L mol}^{-1}\ \text{s}^{-1}$$