***Chemistry***

**12: Kinetics**

**12.3: Rate Laws**

13. 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 22 = 4.

;

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



15. How much and in what direction will each of the following affect the rate of the reaction:  if the rate law for the reaction is ?

(a) Decreasing the pressure of NO2 from 0.50 atm to 0.250 atm.

(b) Increasing the concentration of CO from 0.01 *M* to 0.03 *M*.

Solution

(a) 

Since Rate1 is four times as large as Rate2, 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.

17. 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  is first order with respect to both NO and O3 with a rate constant of 2.20  107 L/mol/s. What is the instantaneous rate of disappearance of NO when [NO] = 3.3  10–6 *M* and [O3] = 5.9  10–7 *M*?

Solution

Rate = *k*[NO][O3] = 2.20  107 L/mol/s[3.3  10–6 *M*][5.9  10–7 *M*] = 4.3  10–5 mol/L/s

19. The rate constant for the radioactive decay of 14C is 1.21  10–4 year–1. The products of the decay are nitrogen atoms and electrons (beta particles):



rate = 

What is the instantaneous rate of production of N atoms in a sample with a carbon–14 content of 6.5  10–9 *M*?

Solution

rate = 1.21  10–4 year–1 [6.5  10–9 *M*] = 7.9  10–13 mol/L/year

21. 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:

|  |  |  |  |
| --- | --- | --- | --- |
| [C2H5OH] (*M*) | 4.4  10–2 | 3.3  10–2 | 2.2  10–2 |
| Rate (mol/L/h) | 2.0  10–2 | 2.0  10–2 | 2.0  10–2 |

Table 12.4

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

Solution

The rate is independent of the concentration. Therefore, rate = *k*;*k* = 2.0  10–2 mol/L/h (about 0.9 g/L/h for the average male); The reaction is zero order—that is, it does not depend on the concentration of any reagent.

23. Nitrosyl chloride, NOCl, decomposes to NO and Cl2.



Determine the rate equation, 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/h) | 8.0  10–10 | 3.2  10–9 | 7.2  10–9 |

Table 12.6

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 equation give:

Experiment 1: 8.0  10–10 mol/L/h = *k*[0.10 mol/L]*m*

Experiment 2: 3.20  10–9 mol/L/h = *k*[0.20 mol/L]*m*

Experiment 3: 7.2  10–9 mol/L/h = *k*[0.30 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:



rate = *k*[NOCl]2; *k* = 8.0 × 10–8 L/mol/h; second order

25. Nitrogen monoxide reacts with chlorine according to the equation:



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

|  |  |  |
| --- | --- | --- |
| [NO] (mol/L1) | [Cl2] (mol/L) | Rate (mol/L/h) |
| 0.50 | 0.50 | 1.14 |
| 1.00 | 0.50 | 4.56 |
| 1.00 | 1.00 | 9.12 |

What is the rate equation that describes the rate’s dependence on the concentrations of NO and Cl2? What is the rate constant? What are the orders with respect to each reactant?

Solution

The rate law has the general form:



Comparing the data in rows 1 and 2, [Cl2] 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, [Cl2] doubles, and the rate doubles, so *n* = 1. The rate equation is:



Data from row 1 are used to determine *k*.



; second order in NO; first order in Cl2]

27. For the reaction , the following data were obtained at 30 °C:

|  |  |  |  |
| --- | --- | --- | --- |
| [*A*] (*M*) | 0.230 | 0.356 | 0.557 |
| Rate (mol/L/s) | 4.17  10–4 | 9.99  10–4 | 2.44  10–3 |

Table 12.9

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

(b) What is the rate constant?

Solution

(a) The rate equation 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*):



Taking the natural log of each side gives:

ln 0.4174 = *m*(ln 0.230) – *m*(ln 0.356)

–0.8737 = –1.4697*m* + 1.0328*m*

–0.8737 = –0.4369*m*

**

Therefore, the rate equation 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 equation in conjunction with data found by substituting any of the three sets of data into the rate equation. Using the data from Equation 1 gives:

4.17  10–4 mol/L/s = *k*[0.230 *M*]2



29. The rate constant for the first–order decomposition at 45 °C of dinitrogen pentoxide, N2O5, dissolved in chloroform, CHCl3, is 6.2  10–4 min–1.



What is the rate of the reaction when [N2O5] = 0.40 *M*?

Solution

(a) The rate of reaction for a first-order reaction in N2O5 is written as rate = *k*[N2O5] where *k*, the rate constant at 45 °C, is 6.2  10–4 min–1. When [N2O5] = 0.40 *M*,

rate = 6.2  10–4 min–1 (0.40 mol/L) = 2.5  10–4 mol/L/min

31. The following data have been determined for the reaction:



|  |  |  |  |
| --- | --- | --- | --- |
|  | 1 | 2 | 3 |
| (*M*) | 0.10 | 0.20 | 0.30 |
| (*M*) | 0.050 | 0.050 | 0.010 |
| Rate (mol/L/s) | 3.05  10–4 | 6.20  10–4 | 1.83  10–4 |

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

Solution

The rate equation 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  10–4 = *k*[0.10]1[0.05]*n*  3.05  10–3 = *k*[0.05]*n*

1.83  10–4 = *k*[0.30]1[0.01]*n*  6.1  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 equation:



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