The rate Law

- From the previous point we learned that:
- The rate of a reaction is proportional to the concentration of reactants and that the proportionality constant (K) is called the rate constant.
- The rate Law expresses the relationship of the rate of a reaction to the rate constant and the concentrations of the reactants raised to some powers.
- For the general reaction

$$aA + bB \longrightarrow cC + dD$$

- The rate Law takes the form

$$\text{Rate} = K[A]^x[B]^y \longrightarrow (1)$$

x,y → numbers that must be determined experimentally .

x,y → are not equal to the stoichiometric coefficients a and b

- Reaction order: → the sum of powers to which all reactant concentrations appearing in the rate Law.

1st order, 2nd order ,3rd order and zero order.

- From equation (1) we can say that:

1) The reaction is Xth order in A.

2) Yth order in B.

3) (X+Y)th the overall order.

☒ Let's determine the rate Law of the reaction between fluorine and chlorine dioxide.

$$F_{2\,(g)} + 2ClO_{2\,(g)} \rightarrow 2FClO_{2\,(g)}$$

- This table show three rate measurements for the formation of $[FClO_2]$

$[F_2]$ (*M*)	$[ClO_2]$ (*M*)	Initial Rate (*M*/s)
1. 0.10	0.010	1.2×10^{-3}
2. 0.10	0.040	4.8×10^{-3}
3. 0.20	0.010	2.4×10^{-3}

- From this table we see that
- As we double $[F_2]$ while holding $[ClO_2]$ the reaction rate doubles.

∴The rate is directly proportional to $[F_2]$

"From entries 1 and 2".

- As we quadruple $[ClO_2]$ at constant $[F_2]$→ the rate increases by four times.

∴The rate is also directly proportional to $[ClO_2]$.

- So, we can summarize our observation by writing the rate Law as:-

$$\text{Rate} = K\,[F_2][ClO_2]$$

- Because both $[F_2]$and $[ClO_2]$are raised to the first power.

∴The reaction is first order in $[F_2]$, first order in$[ClO_2]$

and (1+1) and second order overall.

Note that

- $[ClO_2]$ is raised to the power of 1 where as its stoichiometric coefficient in the overall equation is 2.
- From the reactant concentration and the initial rates we can also calculate the rate constant.

Using the first entry of data in the previous table, we can write

$$K = \frac{\text{Rate}}{[F_2][ClO_2]} = \frac{1.2 * 10^{-3} M/S}{0.1M * 0.01M} = 1.2M^{-1}.S^{-1}$$

Example

For the general reaction:

aA+bB → cC+dD

If we have x=1 and y=2, What is the rate Law of the reaction?!

Rate = $K[A]^x[B]^y$

Rate = $K[A][B]^2$

This reaction is first order in A , second order in B and third order overall (1+2=3).

Example

For a certain reaction:

aA+bB → cC+dD

If we have x =0 and y =1, what is the rate Law of the reaction?!

Rate = $K[A]^x[B]^y$

Rate = $K[A]^0[B]^1$

Rate = $K[B]$

This reaction is zero order in A , first order in B and first order overall.

Note that

- The exponent zero tells us that the rate of this reaction is independent on the concentration of A.

The following points summarize our discussion of the rate Law:

1) Rate Laws are always determined experimentally; from the concentrations of reactants and initial reaction rates we can determine the reaction order and then the rate constant of the reaction.

2) Reaction order is always defined in terms of reactant not product concentrations.

3) The order of a reactant is not related to the stoichiometric coefficient of the reactant in the overall balanced equation.

Example

The reaction of nitric oxide with hydrogen at 1280°C is

$2NO_{(g)} + 2H_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(g)}$

From the following data collected at this temperature, determine:

(a) The rate law,

(b) The rate constant, and (c) The rate of the reaction when:

[NO] = 12.0 *10^{-3} *M*

And $[H_2]$ = 6.0 *10^{-3} *M*.

Experiment	[NO] (*M*)	$[H_2]$ (*M*)	Initial Rate (*M*/s)
1	5.0×10^{-3}	2.0×10^{-3}	1.3×10^{-5}
2	10.0×10^{-3}	2.0×10^{-3}	5.0×10^{-5}
3	10.0×10^{-3}	4.0×10^{-3}	10.0×10^{-5}

Solution

(a) Experiments 1 and 2 show that when we double the concentration of NO at constant concentration of H_2, the rate quadruples.

Taking the ratio of the rates from these two experiments:

$$\frac{rate2}{rate1} = \frac{5.0 * 10^{-5} M/s}{1.3 * 10^{-5} M/s} \approx 4 = \frac{k(10.0 * 10^{-3} M) * (2.0 * 10^{-3} M)^y}{k(5.0 * 10^{-3} M) * (2.0 * 10^{-3} M)^y}$$

Therefore,

$$\frac{(10.0 * 10^{-3} M)^x}{(5.0 * 10^{-3} M)^x} = 2^x = 4$$

or $x = 2$, that is, the reaction is second order in NO.

Experiments 2 and 3 indicate that doubling $[H_2]$ at constant [NO] doubles the rate.
Here we write the ratio as:

$$\frac{\text{rate3}}{\text{rate2}} = \frac{10.0 * 10^{-5}\text{M/s}}{5.0 * 10^{-5}\text{M/s}} = 2 = \frac{\text{k}(10.0 * 10^{-3}\text{M}) * (4.0 * 10^{-3}\text{M})^y}{\text{k}(10.0 * 10^{-3}\text{M}) * (2.0 * 10^{-3}\text{M})^y}$$

Therefore,

$$\frac{(4.0 * 10^{-3}M)^y}{(2.0 * 10^{-3}M)^y} = 2^y = 2$$

or $y = 1$, that is, the reaction is first order in H_2.
Hence the rate law is given by:

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

which shows that it is a (2 +1) or third-order reaction overall.

(b) The rate constant k can be calculated using the data from any one of the experiments. Rearranging the rate law, we get

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

The data from experiment 2 give us

$$K = \frac{(5.0 * 10^{-5}\text{M/s})}{\left(10.0 * \frac{10^{-3}\text{M}}{\text{s}}\right)^2 (2.0 * 10^{-3}\text{M})} = 2.5 * 10^2 M^2.S$$

(c) Using the known rate constant and concentrations of NO and H_2, we write

rate = $(2.03 * 10^2$ M/s$)$ $(12.0 * 10^{23}\ M)^2(6.0 * 10^{23}\ M)$
= $2.2 * 10^{-4}\ M$/s

Choose

1) Rate of reaction is proportional to ………...

A) Concentration of reactants
B) Concentration of products
C) Rate constant
D) None of them

2) The sum of the powers to which all reactant concentrations appearing in the rate Law is called……….

A) rate of reaction
B) Reaction order
C) Rate constant
D) Both A and C

From this reaction rate = $K[A]^1[B]^2$

3) This reaction is ……. order in A.

A) first
B) second
C) third
D) zero

4) The above reaction is………order in B.

A) first
B) second
C) third
D) zero

5) The overall order of the above reaction is………

A) first
B) second
C) third
D) zero

6) For the general reaction aA+bB→cC+dD If we have x=1 and y=2 , the rate Law of the reaction is equal………

A) Rate = $K[A][B]$

C) Rate = $K[A][B]^2$

B) Rate = $K[A]^2[B]^1$

D) Rate = $K[A]$

7) For the general reaction aA+bB→cC+dD If we have x =1 and y =0 , the rate Law of the reaction is equal………

A) Rate = $K[A][B]$

C) Rate = $K[A]$

B) Rate = $K[B]$

D) none of them

8) The exponent zero tells us that the rate of the reaction is ………. On the concentration of the reactant.

A) dependent

B) independant

9) If the rate is " Rate = $K[A][B]^2$ " this means that……….

A) This reaction is first order with respect to A

C) This reaction is second order with respect to B

B) This reaction is third order with respect to overall reaction.

D) All of the above

10) For the hypothetical reaction A + 3B → 2C, the rate of appearance of C given by (Δ[C]/Δt) may also be expressed as

A) Δ[C]/Δt = Δ[A]/Δt

C) Δ[C]/Δt = -(2/3) Δ[B]/Δt

B) Δ[C]/Δt = -(3/2) Δ[B]/Δt

D) Δ[C]/Δt = -(1/2) Δ[A]/Δt

11) For the overall chemical reaction shown below, which one of the following statements can be rightly assumed?

$2H_2S(g) + O_2(g) \rightarrow 2S(s) + 2H_2O(l)$

A) The reaction is third-order overall.

B) The reaction is second-order overall

C) The rate law is, rate = $k[H_2S][O_2]$.

D) The rate law cannot be determined from the information given.

12) The reaction" A + 2B → *products*" has been found to have the rate law, rate = $k[A][B]^2$. While holding the concentration of A constant, the concentration of B is increased from *x* to 3*x*. Predict by what factor the rate of reaction increases?

A) 3

B) 6

C) 27

D) 9

13) For the hypothetical reaction A + 3B → 2C, the rate should be expressed as

A) rate = $\Delta[A]/\Delta t$

B) rate = $-3(\Delta[B]/\Delta t)$

C) rate = $(1/2)(\Delta[C]/\Delta t)$

D) rate = $(1/3)(\Delta[B]/\Delta t)$

14) The reaction A + 2B → *products* has the rate law, rate = $k[A][B]^3$. If the concentration of B is doubled while that of A is unchanged, by what factor will the rate of reaction increase?

A) 8

B) 9

C) 4

D) 2

15) The reaction A + 2B → *products* was found to have the rate law, rate = k[A] $[B]^2$. Predict by what factor the rate of reaction will increase when the concentration of A is doubled and the concentration of B is also doubled.

A) 4
B) 2
C) 8
D) 9

16) The reaction A + 2B → *products* was found to follow the rate law, rate = k$[A]^2$[B]. Predict by what factor the rate of reaction will increase when the concentration of A is doubled, the concentration of B is tripled, and the temperature remains constant.

A) 5
B) 6
C) 12
D) 18

17) Appropriate units for a first-order rate constant are

A) M/s.
B) 1/M·s.
C) 1/s
D) $1/M^2$·s

18) It takes 42.0 min for the concentration of a reactant in a first-order reaction to drop from 0.45 M to 0.32 M at 25°C. How long will it take for the reaction to be 90% complete?

A) 13.0 min
B) 86.0 min
C) 137 min
D) 284 min

19) Nitric oxide gas (NO) reacts with chlorine gas according to the equation

$NO + ½Cl_2 \rightarrow NOCl$.

The following initial rates of reaction have been measured for the given reagent concentrations.

Expt. #	Rate (M/hr)	NO (M)	Cl_2 (M)
1	1.19	0.50	0.50
2	4.76	1.00	0.50
3	9.58	1.00	1.00

Which of the following is the rate law (rate equation) for this reaction?

A) rate = k[NO]

B) rate = $k[NO][Cl_2]^{1/2}$

C) rate = $k[NO][Cl_2]$

D) rate = $k[NO]^2[Cl_2]$

20) Use the following data to determine the rate law for the reaction

$2NO + H_2 \rightarrow N_2O + H_2O$.

Expt. #	$[NO]_0$	$[H_2]_0$	Initial rate
1	0.021	0.065	1.46 M/min
2	0.021	0.260	1.46 M/min
3	0.042	0.065	5.84 M/min

A) rate = k[NO]

B) rate = $k[NO]^2$

C) rate = $k[NO][H_2]$

D) rate = $k[NO]^2[H_2]$

21) The data below were determined for the reaction $S_2O_8^{2-} + 3I^-(aq) \rightarrow 2SO_4^{2-} + I_3^-$.

Expt. #	$[S_2O_8^{2-}]$	$[I^-]$	Initial Rate
1	0.038	0.060	1.4×10^{-5} M/s
2	0.076	0.060	2.8×10^{-5} M/s
3	0.076	0.030	1.4×10^{-5} M/s

The rate law for this reaction must be:

A) Rate = k $[S_2O_8^{2-}][I^-]^3$.

B) Rate = k $[S_2O_8^{2-}]$.

C) Rate = k $[S_2O_8^{2-}][I^-]$.

D) Rate = k $[I^-]$.