Chem Factsheet

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# Answering Exam Questions: Rates of Reaction

First, try deciding whether the following statements are true or false:

| | Statement | True | False |
|---|---|---|---|
| 1 | The rate is always proportional to the concentration of a reactant | | |
| 2 | Overall order of reaction is the power to which the concentration of a reactant is raised in the rate equation | | |
| 3 | Increasing the concentration of a reactant does not alter the rate constant | | |
| 4 | The order of a reaction with respect to a reactant is the power to which the concentration of that reactant is raised in the rate equation | | |
| 5 | The rate constant is different for each reactant | | |
| 6 | The orders of reactions with respect to reactants can be used to provide information about the rate determining step of a reaction | | |
| 7 | A large excess of an ionic species may result in it becoming zero order in the rate equation | | |
| 8 | Altering the temperature at which the reaction takes place alters the rate constant | | |

Statements 3, 4, 6, 7 and 8 are true, the others are false. If you were not sure about any of these then it is well worth studying (and learning) all the basic definitions and ideas related to reaction rate. Try reading Factsheet Number 43.

In general, students perform well on this topic. However, this depends very much on:

### A) Three aspects which are primarily mathematical:

**1) Ability to rearrange an equation, namely the rate equation**

If Rate = k $[A]^x [B]^y [C]^z$

$$\text{then } k = \frac{\text{Rate}}{[A]^x [B]^y [C]^z}$$

> ***Extract from Examiners' Report:*** *'Disappointing numbers of candidates failed to rearrange the equation correctly to produce k as the subject.'*

If this proves a problem then it is well worth learning and practising the rearrangement. (Any error here will normally result in the loss of two marks!)

Remember that x, y and z can equal 0, 1 or 2 and if the value is 0 then this is not normally included in the rate equation, as it means that that reactant has no effect on the rate.

**2) Ability to deal with powers of ten correctly**

$$10^{-x} = \frac{1}{10^x}$$

To deal with powers of ten, it is often worthwhile applying a mental check on an answer from a calculator to make sure it is *reasonable* - that is, of the correct order.

e.g. multiplying by a negative power of ten *cannot* produce an answer which is bigger).

> ***Extract from Examiners' Report:*** *'One of the main errors was carelessness with powers of ten.'*

**3) Using the correct number of decimal places**

Remember, that if a question asks for two decimal places for your answer then, the *examiner expects a rounded answer* rather than a truncated one - a truncated answer will gain zero marks. Also you will be penalised for any answer which is not to two decimal places.

### B) Appreciating why changing the concentration of a species which is already in a large excess does not change rate

This is because any changes in the concentration of the reactant during the reaction are *not significant*, and so the concentration is effectively remaining unchanged.

> ***Extract from Examiners' Report:*** *Referring to a question which required the student to explain why "use of high concentrations of NaOH results in [NaOH] appearing to be of zero order in the rate equation" - 'Very few candidates were able to explain this point'*

### C) The effect of temperature on the rate constant, k

An increase in temperature increases the rate of reaction, and so, if the temperature is increased / decreased, the rate constant increases / decreases.

### D) Changing the concentration of a reactant does not change the rate constant.

See if you can work out your own answer to each of the following, and then compare your answers with the student's attempts and the comments. Finally look at the mark scheme and make sure you can understand where and why marks are awarded.

## Sample Student's Worked Question No 1

**Question**

The following data were obtained in a series of experiments where the initial rate of reaction between an ester X and aqueous sodium hydroxide was measured at constant temperature.

| Experiment | Initial concentration of X / mol $dm^{-3}$ | Initial concentration of NaOH / mol $dm^{-3}$ | Initial rate /mol $dm^{-3}s^{-1}$ |
|---|---|---|---|
| 1 | 0.050 | 0.040 | $3.6 \times 10^{-4}$ |
| 2 | 0.050 | 0.060 | $5.4 \times 10^{-4}$ |
| 3 | 0.075 | 0.040 | $5.4 \times 10^{-4}$ |
| 4 | 0.100 | 0.070 | |

Using the data given in the table calculate the order with respect to X and the order with respect to NaOH.

Calculate the initial rate of reaction in Experiment 4. (3 marks)

In a further series of experiments at a different temperature, the concentration of NaOH was increased to 2.00 mol $dm^{-3}$. The reaction was first order with respect to X and appeared to be zero with respect to NaOH.

Write down the rate equation under these conditions and explain why the reaction appears to be zero order with respect to NaOH. (2 marks)

If the initial rate of reaction was found to be 8.0 x $10^{-3}$ mol $dm^{-3}$ $s^{-1}$ when the initial concentration of X was 0.030 mol $dm^{-3}$, calculate the new value for the rate constant. (3 marks)

***Student's Answer***

*1st order with respect to X*
*2nd order with respect to NaOH*
*Initial rate in Experiment 4 was $1.26 \times 10^{-3}$*
*Rate equation is rate = k[X][NaOH]*

*The temperature was lower and the reaction was slower, so the NaOH seemed to have less effect.*

*$k = [X][NaOH] \div rate = 0.030 \times 2.00 \div 8.0 \times 10^{-3} = 0.0075 \times 10^{-3}$*

**Comments on this Answer**

The first mark is gained but second lost.

The rate is correct so the third mark is awarded - the units are given in the table and need not be repeated.

It is important if possible to find the data which keeps the concentration of one reactant constant when calculating the order of the other reactant.

The rate equation is wrong since it applies to the first set of experiments. Also, it contradicts the student's answers for the first 2 parts!

The explanation is incorrect.

The equation is incorrectly rearranged, the maths is incorrect and there are no units - hence, no marks are gained.

Note: An incorrectly arranged equation together with correct maths can often be *spotted* as incorrect, due to the value of the rate being much too high! Also remember that this is a rate so it must include the units of $time^{-1}$. Correct units may be credited even with incorrect or no working.

**Mark Scheme**

1st order (1 mark)
1st order (1 mark)
Rate = $1.26 \times 10^{-3}$ (1 mark)
Rate equation Rate = k[X] (1 mark)
$[OH^-]$ is large / high and so $[OH^-]$ is effectively constant. (1 mark)

$k = \frac{8.0 \times 10^{-3}}{0.02}$ (1 mark)

$= 0.40\ s^{-1}$ (1 mark) + (1 mark)

## Sample Student's Worked Question No 2

**Question**

The initial rate of the reaction at constant temperature between two compounds A and B was recorded and the following rate equation obtained

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

Fill in the gaps in the following table for the reaction between A and B. (3 marks)

| Experiment | Initial [A] / mol dm$^{-3}$ | Initial [B] / mol dm$^{-3}$ | Initial rate / mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 1 | $4.0 \times 10^{-3}$ | $1.0 \times 10^{-3}$ | $1.60 \times 10^{-5}$ |
| 2 | $4.0 \times 10^{-3}$ | | $6.40 \times 10^{-5}$ |
| 3 | $2.0 \times 10^{-3}$ | $1.0 \times 10^{-3}$ | |
| 4 | | $0.4 \times 10^{-3}$ | $5.76 \times 10^{-5}$ |

Using the data from experiment 1, calculate a value for the rate constant, k, including its units. (3 marks)

***Student's Answer***

| Experiment | Initial [A] / mol dm$^{-3}$ | Initial [B] / mol dm$^{-3}$ | Initial rate / mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 1 | $4.0 \times 10^{-3}$ | $1.0 \times 10^{-3}$ | $1.60 \times 10^{-5}$ |
| 2 | $4.0 \times 10^{-3}$ | **$4.0 \times 10^{-3}$** | $6.40 \times 10^{-5}$ |
| 3 | $2.0 \times 10^{-3}$ | $1.0 \times 10^{-3}$ | **$0.80 \times 10^{-5}$** |
| 4 | **$4.5 \times 10^{-3}$** | $0.4 \times 10^{-3}$ | $5.76 \times 10^{-5}$ |

*Rate constant =* $k = [A]^2[B] \div rate = 4.0 \times 10^{-3} \times 1.0 \times 10^{-3} \div 1.6 \times 10^{-5}$

$= 4.0 \div 1.6 \times 10^{-5} \times 10^{-3} \times 10^{-3}$

$= 2.5$ *mol dm* $^{-3}$ *s* $^{-1}$

**Comments on this Answer**

The first mark is gained but the answers for experiments 3 and 4 are wrong. Experiment 3 and 4 are calculated as if the order of [A] is 1 rather than 2.

Note: If a reactant is of order 2 in the rate equation, then halving its concentration reduces the rate by a factor of a quarter.

Note: It is important to note that the answers to 3 and 4 should be calculated using experiment 1, rather than student calculated data.

The student's rearrangement of the equation is incorrect and the student also subsequently fails to square [A]. The units are also incorrect.

Note: As the rate constant depends directly on the rate but inversely on the concentrations, the units must be of the form mol$^{-x}$dm$^{y}$s$^{-1}$. The actual values of x and y depend on the rate equation, but the ratio of x to y is always 1 : 3.

**Mark Scheme**

| Experiment | Initial [A] / mol dm$^{-3}$ | Initial [B] / mol dm$^{-3}$ | Initial rate / mol dm$^{-3}$ s$^{-1}$ |
|---|---|---|---|
| 1 | $4.0 \times 10^{-3}$ | $1.0 \times 10^{-3}$ | $1.60 \times 10^{-5}$ |
| 2 | $4.0 \times 10^{-3}$ | **$4.0 \times 10^{-3}$** | $6.40 \times 10^{-5}$ |
| 3 | $2.0 \times 10^{-3}$ | $1.0 \times 10^{-3}$ | **$0.40 \times 10^{-5}$** |
| 4 | **$12.0 \times 10^{-3}$** | $0.4 \times 10^{-3}$ | $5.76 \times 10^{-5}$ |

Rate constant, k $= 1.6 \times 10^{-5} \div [(4.0 \times 10^{-3})^2 (1.0 \times 10^{-3})]$ (1 mark)

$= 1000$ mol$^{-2}$dm$^{6}$s$^{-1}$ (2 marks)

## Sample Student's Worked Question No 3

**Question**
In a study of the rate of reaction at constant temperature between compounds A, B, and C the following data table was obtained.

| Experiment | $[A]_{Initial}$ /mol $dm^{-3}$ | $[B]_{Initial}$ /mol $dm^{-3}$ | $[C]_{Initial}$ /mol $dm^{-3}$ | Initial rate/mol $dm^{-3}s^{-1}$ |
|---|---|---|---|---|
| 1 | 0.30 | 0.10 | 0.20 | $0.60 \times 10^{-3}$ |
| 2 | 0.30 | 0.40 | 0.20 | $2.40 \times 10^{-3}$ |
| 3 | 0.15 | 0.80 | 0.20 | $1.20 \times 10^{-3}$ |
| 4 | 0.15 | 0.60 | 0.10 | $0.90 \times 10^{-3}$ |

Find the order of the reaction with respect to compounds A, B, and C. (3 marks)
Write down the rate equation (1 mark)

***Student's Answer***
*Order of reaction with respect to A is ½ x 2 = 1*
*Order of reaction with respect to B is ¼ concentration causes ¼ of rate = order 1*
*Order of reaction with respect to C is ½ concentration causes 0 .375 of rate = 2*
*rate = k [A][B]* $[C]^2$

**Comments on this Answer**
Only the order of reaction with respect to B is correct, but the student has followed through correctly to give his/her correct rate equation and so gains two marks total.

Using experiments 1 and 2: It is important to *calculate the order for B first* where the concentrations of A and C are constant. Then apply the change in B to the rate first and use this to calculate the orders of A or C as follows:

Using experiments 2 and 3: B is order 1 so doubling B *alone* would double the rate to $4.80 \times 10^{-3}$.
However, the effect of halving A is to cause the rate to go down to $1.20 \times 10^{-3}$ which means halving A causes the rate to be ¼. Hence, A is order 2.

Using experiments 3 and 4: Reducing the concentration of B by ¾ causes the rate to fall to ¾. Hence, since B is order 1, C is not having any effect and so is order 0.

**Mark Scheme**

Order with respect to A is 2 (1 mark)

Order with respect to B is 1 (1 mark)

Order with respect to C is 0 (1 mark)

Rate = k $[A]^2$ [B] (1 mark)

or Rate = k $[A]^2$ [B] $[C]^0$ is accepted provided zero is shown.

## Practice Questions

1. The rate equation for a reaction between compounds A and B at a T°C is: Rate = k $[A]^2$ [B]
If the initial rate of reaction is $9.32 \times 10^{-4}$ mol $dm^{-3}$ $s^{-1}$ when the initial concentrations of A and B are 0.72 mol $dm^{-3}$ and 1.24 mol $dm^{-3}$ respectively.
Calculate a value for the rate constant, k at this temperature and deduce its units. (3 marks)

2. The following table gives the results of three experiments carried out at constant temperature.

| Experiment | Initial concentration of X / mol $dm^{-3}$ | Initial concentration of Y / mol $dm^{-3}$ | Initial rate / mol $dm^{-3}$ $s^{-1}$ |
|---|---|---|---|
| 1 | 0.60 | 0.24 | $8.60 \times 10^{-3}$ |
| 2 | 0.30 | 0.24 | $2.15 \times 10^{-3}$ |
| 3 | 0.30 | 0.48 | $4.30 \times 10^{-3}$ |

Deduce the order with respect to X and the order with respect to Y. (2 marks)

3. (a) In a reaction between two compounds A and B at a given temperature $T_1$, the order of reaction with respect to A is two and the order of reaction with respect to B is one. The rate constant at temperature $T_1$ is $5.6 \times 10^{-4}$ $mol^{-2}$ $dm^6$ $s^{-1}$.
Write a rate equation for the reaction and calculate a value for the initial rate of reaction when the initial concentrations of A and B are 0.24 mol $dm^{-3}$ and 0.72 mol $dm^{-3}$ respectively. (3 marks)
(b) In a second experiment at temperature $T_2$ the initial rate of reaction is $8.84 \times 10^{-5}$ mol $dm^{-3}$ $s^{-1}$ when the initial concentrations of A are 0.74 mol $dm^{-3}$ and 0.96 mol $dm^{-3}$ respectively. Calculate the value of the rate constant at $T_2$ .
(c) From your answer, deduce which is the higher temperature, $T_1$ or $T_2$. (3 marks)

## Answers

1. Value of k = rate ÷ $[A]^2$ [B] = $\frac{9.32 \times 10^{-4}}{(0.72)^2 (1.24)}$ (1 mark)
= $1.45 \times 10^{-3}$ (1 mark)
Units of k are $mol^{-2}$ $dm^6$ $s^{-1}$ (1 mark)

2. Order with respect to X = 2 (1 mark)
Order with respect to Y = 1 (1 mark)

3. (a) Rate = k $[A]^2$ [B] (1 mark)
Initial rate of reaction = $5.6 \times 10^{-4} \times (0.24)^2 \times 0.72$ (1 mark)
= $2.32 \times 10^{-5}$ mol $dm^{-3}s^{-1}$ (1 mark)
(b) k = $\frac{8.84 \times 10^{-5}}{(0.74)^2 (0.96)}$ (1 mark)
= $1.68 \times 10^{-4}$ $mol^{-2}$ $dm^6s^{-1}$ (1 mark)
(c) $T_1$ is the higher temperature because k increases as temperature increases (1 mark)

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