King's College London (KQC) University of London

SCIENCE SIMULATIONS LABORATORY

CHEMICAL REACTION KINETICS

STUDENTS' MANUALS (Version 1.02.2003)

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STUDENTS' MANUAL A – INTRODUCTION

Aim

This unit makes use of a computer program in which a series of mathematical equations, a mathematical model, represents the ways in which various factors influence the rate of chemical reactions. The use of a model is frequently referred as a 'simulation' as the model attempts to represent or simulate what would happen in reality.

The purpose of this simulation unit is to widen your experience and understanding of reaction kinetics. It is not intended in any way to replace laboratory experiment but to complement and extend that work. The simulation model is based on data from real experiments which took place in laboratories. Some of these experiments are difficult to perform and require special facilities. By using the computer model it is possible to investigate a variety of reactions, and the effects of changes in temperature and concentration. The use of the simulation also provides experience in selecting reaction conditions which produce meaningful results.

More specifically it is intended that through the study of first order and equal concentration second order reactions, the unit should help you understand:

a the effect on the rate of a reaction of changing the initial concentrations or the temperature;

b what the value of the rate constant means in terms of a reaction;

c the fact that the order cannot be inferred directly from the equation for the overall reaction but can only be discovered empirically;

d the use of a mathematical model and its connection with reality.

The order of a reaction

For many chemical reactions, it is found experimentally that the way in which the concentrations of reactants (and sometimes species other than those appearing in the equation) affect the rate of a reaction can be expressed in the form of simple law.

First order reaction

For the reaction $2N_2O(g) \rightarrow 2N_2(g) + O_2(g)$

the law is Rate $\propto$ $[N_2O]$

or, as the concentration is decreasing Rate = $-k\ [N_2O]$ (where square brackets indicate concentration and k is the rate constant)

The reaction is said to be first order with respect to N_2O (in the rate equation the concentration is only raised to the first power). As this is the only substance affecting the rate, the reaction is said to be first order overall. For first order reactions, although there may be more than one substance on the left hand side of the chemical equation, or the one substance may have a stoichiometric coefficient other than one, the rate is proportional only to the concentration of one substance on the left-hand side.

Second order reaction

For the following reaction, where acid is present:

$$CH_3COCH_3(aq) + I_2(aq) \;\;(\;\; CH_3COCH_2I + H^+(aq) + I^-\,(aq)$$

the law is $\qquad$ Rate $\propto$ $[CH_3COCH_3]$ x $[H^+]$

or, as the concentration is decreasing

$$\text{Rate} = -k\,[CH_3COCH_3] \times [H^+]$$

The reaction is said to be first order with respect to acetone (as the concentration of acetone appears in this rate equation to the power one), first order with respect to hydrogen ions (concentration of hydrogen ions also to the power one), and thus second order overall.

For second order reactions, the rate is proportional either to the concentration of one substance to the power two or to the product of the concentration of two substances to the power one. These two substances need not both appear on the left hand side of the chemical equation as shown in this example.

The rate constant k

There is a value of k for each temperature T, of a chosen reaction. For most reactions the relation is given by the Arrhenius equation:

$$K = A\exp\left(\frac{-E}{RT}\right)$$

where E is the Activation Energy and A the pre-exponential factor for that reaction.

R is constant for all such reactions

Thus for the decomposition of N_2O above:

$$R = A\exp\left(\frac{-E}{RT}\right)[N_2O]$$

This equation forms the model used in the simulation of the decomposition of N_2O.

STUDENTS' MANUAL B – USING THE PROGRAM WITH YOUR OWN DATA

Suppose you have done an experiment in the laboratory and obtained a table of results giving eight concentrations and times. Analysis of these showed that it was a second order reaction having a rate constant of 0.2. Your data for the investigation might be:

Initial concentration	0.33 mol dm^{-3}
Temperature of reactants	293 K assumed constant
Interval between readings	10 s
Reaction number	1
Number of readings	8
Order of reaction	Second order
Rate constant	0.2 $dm^3mol^{-1}s^{-1}$

You will be able to find out whether the computer gives you approximately the same results as those which you obtained in your investigation, that is whether the mathematical model in the computer program simulates reasonably accurately the kinetics of the reaction.

The results on the screen will be:

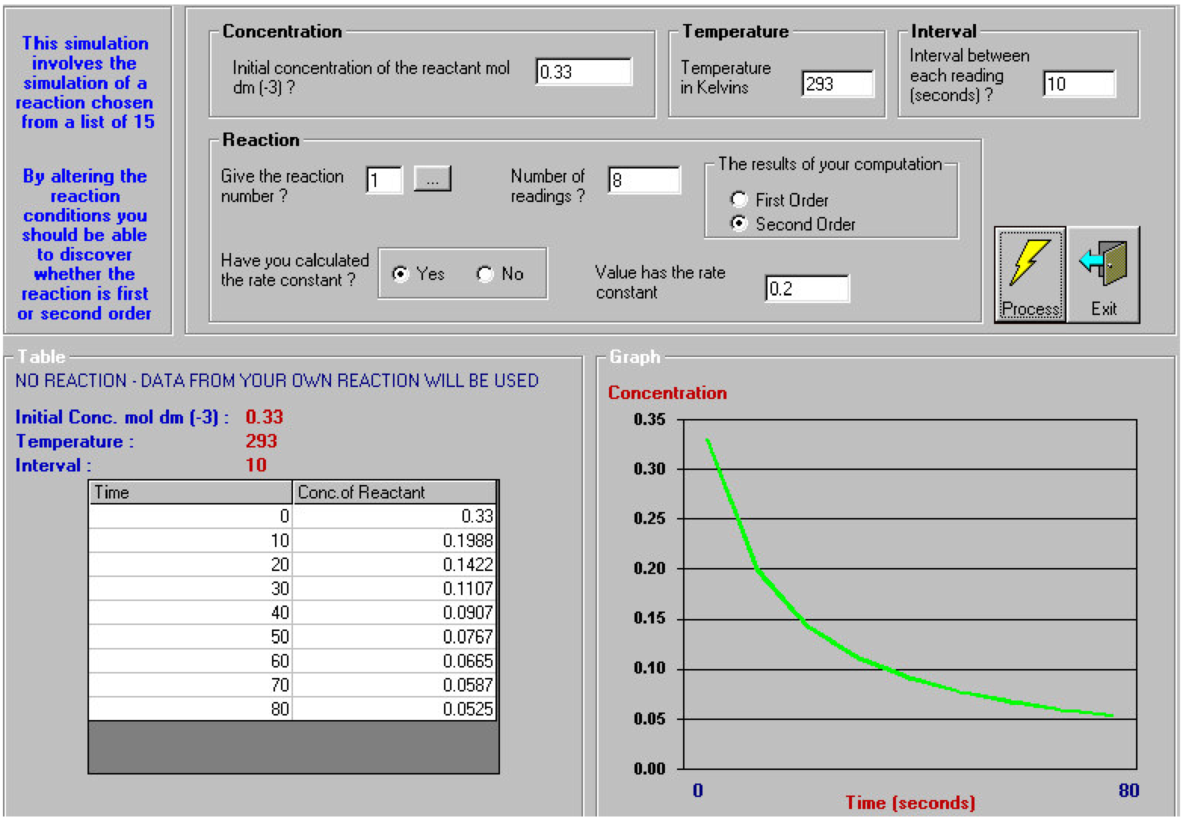


Figure B1

Calculation

The calculation referred to in the example might have been done in the following way. If your reaction was of the form

$$A + B \rightarrow C$$

and you began with equal concentrations of A and B you might be able to see that

$$\text{rate} = -k\,[A]\,[B]$$

or that rates plotted against the product of concentrations gave a straight line.

By finding rates at different concentrations or from the slope of the line it is possible to calculate the value of k at this temperature.

STUDENTS' MANUAL C – SIMULATED REACTIONS

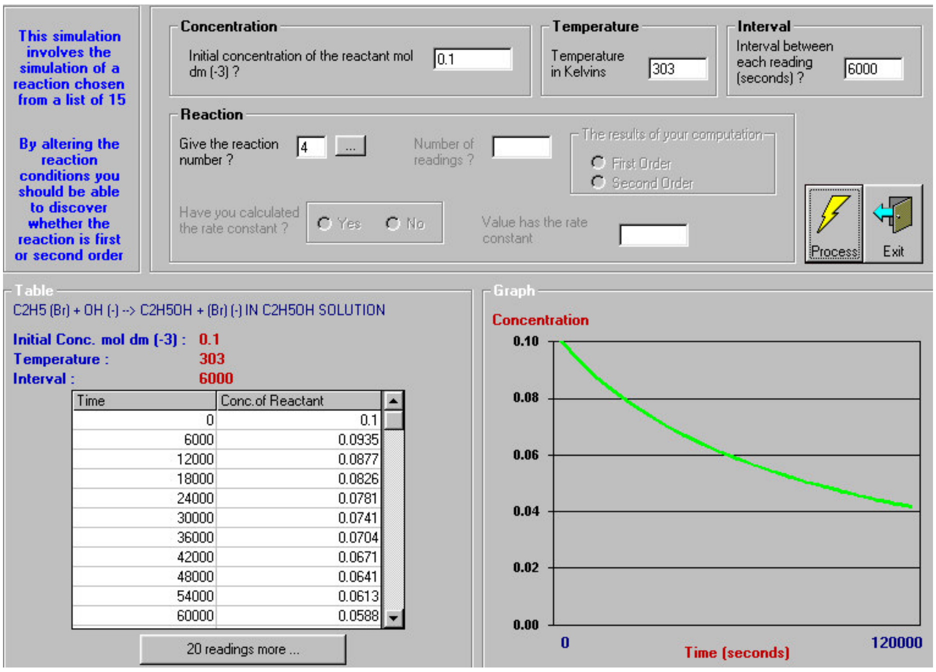
There are 15 reactions available for you to investigate. Suppose that the reaction chosen is:

$C_2H_5Br + OH^- \rightarrow C_2H_5OH + Br^-$ in C_2H_5OH solution (Reaction 4)

A one-tenth molar solution could be chosen and the reaction investigated at about 30°C (303 K). It is known to be ' very slow' (which may mean almost a day) so readings at intervals of 100 minutes (6000 seconds) will be tried. Therefore the data to be supplied to the program is:

Variable	Data
Temperature	303 K
Interval between readings	6000 s
Initial concentration	0.1 mol dm^{-3}
Reaction number	4

Then the computer program will use its mathematical model to calculate the results, giving some output like this:



As you can see from the above copy of the screen you can investigate the influence of temperature and initial concentration on the rate of reaction. Note: for any reaction, the first results you obtain may indicate a much slower or faster reaction than you expected. Try to devise an efficient system of varying the ' Interval Between Readings in Seconds' so as to get results quickly which are suitable for plotting or similar analysis. Now use the program to answer the following questions:

C1 *It is said that ´a rise in temperature of 10 K doubles the rate of reaction'. Use Investigation 14 to see if this is a reasonable approximation for the reaction NO + $Cl_2 \rightarrow$ NOCl + Cl· (Start by selecting temperatures in the range 300-600 K and time intervals of about 500 seconds between readings).*

C2 *The screen graph of your results provides you with sufficient information to answer C1. However, you may not find this format very easy to use. Suggest and try out some other ways of analysing the results.*

C3 *You have performed an investigation (with constant initial concentrations) (C1) to study changes in temperature on reaction rates. Are the results you obtained for that reaction similar to other reactions available to you?*

C4 *What information is needed before you can forecast the order of a reaction?*

C5 *For a series of investigations you will have found various completion times. Does this help you to make forecasts of completion times for other reactions?*

C6 *Choose some of the tables of concentrations obtained from the simulation and find the rate constants for those reactions.*

- *i* *What range do they lie within?*
- *ii* *What do their values mean in terms of the rate of the reaction?*

C7 *Keeping temperature constant, find how changing the initial concentration of the reactants affects the course of the reaction.*

STUDENTS' MANUAL D – THE MODEL USED IN THE SIMULATION

Assumptions in the simulation

Before proceeding further, you should be aware of the basis of the simulation. The computer program has been written using equations referred to below. Experimentally determined chemical constants, and other values which you are able to choose, are substituted into these equations to calculate the predicted concentration of the reactant at later intervals of time as the program runs.

No mathematical model is capable of predicting reality exactly. Complex models may come quite close to this, but often the broad pattern of relationships between parameters in a scientific situation can be seen through the use of simple models. In the formulation of any model assumptions must made; the simpler the model, the broader the assumptions.

The model used in this program incorporates the following assumptions.

1. It is expected that the simulation will be used over the range of conditions which can be achieved experimentally. It cannot be used meaningfully for temperatures at which dissociation of the product molecules occurs or at which the solution boils or freezes.

2. The temperature of the reaction remains constant throughout the reaction.

3. The reaction follows one path only.

4. The reaction follows simple first or second order kinetics to a close approximation.

5. Only one initial concentration can be specified, and for a second order reaction both reagents begin with this concentration. In the laboratory it would be possible, for some second order reactions, to set different initial concentrations for two substances involved in the rate equation, e.g. the reaction where

$$\text{Rate} \propto [CH_3COCH_3] \times [H^+]$$

6. In the case of reversible reactions, all products are removed from the system as they are formed.

Mathematical model

If the concentration of a reactant is C then its rate of change with time is $\frac{dC}{dt}$

and the rate of reaction is $-\frac{dC}{dt}$ as C is decreasing.

First order reaction

$$Rate = -k_1[N_2O]$$
$$\frac{dC}{dt} = -k_1 C$$

The concentration must have the value C_ϕ (the initial concentration) at time zero and is of exponential form because the rate of change of C is proportional to C. The variation in concentration is described by the equation:

$$C = C_\phi \ \exp(-k_1 t) \qquad \text{..................(1)}$$

Second order reaction

$$\text{Rate} = -k_2[CH_3COCH_3]\times[H^+]$$

$$\frac{\text{dC}}{\text{dt}} = -k_2 C^2 \qquad \text{(as concentrations are equal in this model)}$$

$$\int \frac{\text{dC}}{\text{C}^2} = \int -k_2 dt \qquad \text{by integrating}$$

$$\left[\frac{-1}{C}\right]_{C_\phi}^{C} = -t_2[t]_\phi^t \qquad \text{with concentration } C_\phi \text{ at time } \phi$$

or $$\frac{1}{C} - \frac{1}{C_\phi} = k_2 t$$

i.e. $$\frac{1}{C} = \frac{k_2 t C_\phi + 1}{C_\phi}$$

and $$C = \frac{C_\phi}{k_2 t C_\phi + 1} \qquad \text{.......................(2)}$$

Other order reactions

Many reactions obey much more complicated laws. For example the reaction

H_2(g) + Br_2(g) + 2HBr(g) follows the rate law:

$$Rate = \frac{-k[H_2]\times[Br_2]^{1/2}}{1+k_i\left[\frac{HBr}{Br_2}\right]}$$

where k_i is the inhibition constant and *rate* is the change in concentration of HBr

The rate constant

The Arrehenius equation is used to describe the way the rate constant k varies with the absolute temperature T.

$$k = A\exp\left(\frac{-E}{RT}\right) \qquad \text{.................(3)}$$

where A is a constant for the reaction, called the pre-exponential factor
R is the gas constant
and
E is the activation energy for the reaction.

Equation (3) together with (1) or (2) is the basis of the model which is used in the program. The values of E and LnA used for each reaction are given in the Teachers' Notes.

STUDENTS' MANUAL Z – REACTIONS

Simulations of the following reactions are available.

1	The simulation of one of your laboratory experiments.	
2	$2N_2O_5 \rightarrow 4NO_2 + O_2$	in CCl_4 solution
3	$CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$	in aqueous solution
4	$C_2H_5Br + OH^- \rightarrow C_2H_5OH + Br^-$	in C_2H_50H solution
5	$NH^+{}_4 + CNO^- \rightarrow (NH_2)\ {}_2CO$	in aqueous solution
6	$N_2O_4 \rightarrow 2NO_2$	gas
7	$H_2 + I_2 \rightarrow 2HI$	gas
8	$2HI \rightarrow H_2 + I_2$	gas
9	$2N_2O \rightarrow 2N_2 + O_2$	gas
10	$2NOCl \rightarrow 2NO + Cl_2$	gas
11	$CH_3{}^{\cdot} + CH_3{}^{\cdot} \rightarrow C_2H_6$	gas
12	$CH_3CH_2Cl \rightarrow CH_2H_4 + HCl$	gas
13	$CH_3 –N=N–CH_3 \rightarrow C_2H_6 + N_2$	gas
14	$NO + C1_2 \rightarrow NOCl + + Cl$	gas
15	$NOC1 + Cl^{\cdot} \rightarrow C1_2 + NO$	gas
16	$(CH_3)\ 3CBr \rightarrow (CH_3)\ {}_2CCH_2 + HBr$	gas