Modelling chemical reactions: numerical solution of the equation of the reaction rate

$$A \longrightarrow B$$

1. Let's assume that variable A represents the **concentration** of the **reactant** and that variable B the **concentration** of the **product** in the chemical reaction A → B.

2. The **rate of the reaction**, v, is a quantity that measures how fast A is transformed into B.

3. Experimentally one can find which factors influence the rate v. For certain reactions, the **rate** is **proportional** to the concentration A.

4. If it is a direct proportion, $v = k\,A$, where k is a constant of proportionality. This equation is called the **rate law** of the reaction.

5. The **instantaneous rate of change** of reactant A is the **derivative** of the concentration A in order to time, $v = \mathrm{d}A/\mathrm{d}t$. It is possible to compute **approximate values** of the rate of change using small time increments, from t to $t + \Delta t$:

$$v = \frac{\mathrm{d}A}{\mathrm{d}t}$$

$$v \approx \frac{\Delta A}{\Delta t}$$

$$v \approx \frac{A(t+\Delta t) - A(t)}{\Delta t}$$

6. Solving this equation to compute the "new values of A" at instant $t + \Delta t$, $A\,(t + \Delta t)$ knowing the value of A at the previous instant t, $A(t)$, and the rate of change, v, we obtain:

$$v \times \Delta t \approx A(t+\Delta t) - A(t)$$

$$A(t) + v \times \Delta t \approx A(t+\Delta t)$$

$$A(t+\Delta t) \approx A(t) + v \times \Delta t$$

7. The values obtained with this iterative equation are closer and closer to the correct solution as Δt is smaller and smaller (the approximation gets better as time increments Δt gets smaller...)

8. Since the concentration A is decreasing during the reaction, v is negative... In order to avoid the use of negative values, the instantaneous rate of change of A is usually written as $v = -\mathrm{d}A/\mathrm{d}t$. Then, the last iterative equation becomes $A(t + \Delta t) \approx A(t) + (-v \times \Delta t)$.

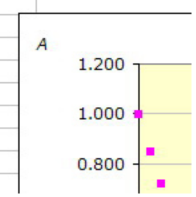
delta_t (parameter Δt)

k (parameter k)

A0 (value of concentration A when time t = 0)

B0 (value of concentration B when time t = 0)

	A	B	C	D	E	F
1						
2		Modelling the first order chemical reaction, A -> B				
3						
4		delta_t=	0.1	time step in seconds		
5		k=	1.5	rate constant		
6		A0=	1	initial concentration of reactant A		
7		B0=	0	initial concentration of reactant B		
8						
9		*t*	*v*	*A*		
10		0.00	1.500	1.000		
11		0.10	1.275	0.850		
12		0.20	1.084	0.723		
13		0.30	0.921	0.614		
14		0.40	0.783	0.522		
15		0.50	0.666	0.444		
16		0.60	0.566	0.377		
17		0.70	0.481	0.321		



= A0

= k*D10

$v = k\;A(t)$

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= D10+(-C10*delta_t)

$A(t+\Delta t) \approx A(t) + (-v \times \Delta t)$

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= B10+delta_t

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Modelling chemical reactions: numerical solution of the equation of the reaction rate in Excel and in Modellus

1. Left, in Excel: the numerical solution of the mathematical model of the reaction rate of the reaction A → B. The change in the concentration *A*, in each step, is ($-v \times \Delta t$). This model uses the iterative equation new value = old value + rate of change × small time interval.

2. Right, in Modellus: the rate law is expressed as a function ($v = k\,A$) and the rate of change is simply the differential equation $dA/dt = -v$.

$$A \longrightarrow B$$

The values obtained with the Modellus model (below) are closer to the exact solution of the differential equation $dA/dt = -k\,A$. On the Excel model (left), changing delta_t to a smaller value, you will get a better approximation. Check it with delta_t = 0.01 (you will need also to "Fill Down" 10 times more cells...).

	A	B	C	D
1				
2		Modelling the first order chemical reaction, A -> B		
3				
4		delta_t=	0.1	time step in seconds
5		k=	1.5	rate constant
6		A0=	1	initial concentration of reactant A
7		B0=	0	initial concentration of reactant B
8				
9		*t*	*v*	*A*
10		0.00	1.500	1.000
11		0.10	1.275	0.850
12		0.20	1.084	0.723
13		0.30	0.921	0.614
14		0.40	0.783	0.522
15		0.50	0.666	0.444
16		0.60	0.566	0.377
17		0.70	0.481	0.321
18		0.80	0.409	0.272
19		0.90	0.347	0.232
20		1.00	0.295	0.197
21		1.10	0.251	0.167
22		1.20	0.213	0.142
23		1.30	0.181	0.121
24		1.40	0.154	0.103
25		1.50	0.131	0.087
26		1.60	0.111	0.074
27		1.70	0.095	0.063
28		1.80	0.080	0.054
29		1.90	0.068	0.046
30		2.00	0.058	0.039
31		2.10	0.049	0.033
32		2.20	[illegible]	0.028
33		2.30	[illegible]	0.024
34		2.40	[illegible]	0.020
35		2.50	[illegible]	0.017
36		2.60	0.022	[illegible]
37		[illegible]	[illegible]	0.012
38		[illegible]	[illegible]	0.011
39		[illegible]	[illegible]	0.009
40		3.00	0.011	0.008

$v = kA$

$\dfrac{dA}{dt} = -v$

$A(t + \Delta t) = A(t) + (-v\Delta t)$

= A0

= k*D10

Edit / Fill Down...

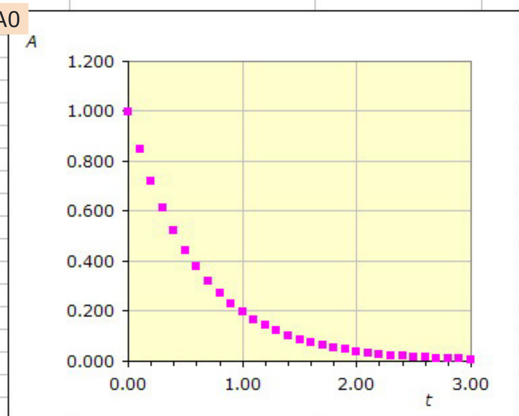
= D10+(-C10*delta_t)

$A(t + \Delta t) \approx A(t) + (-v \times \Delta t)$

Edit / Fill Down...

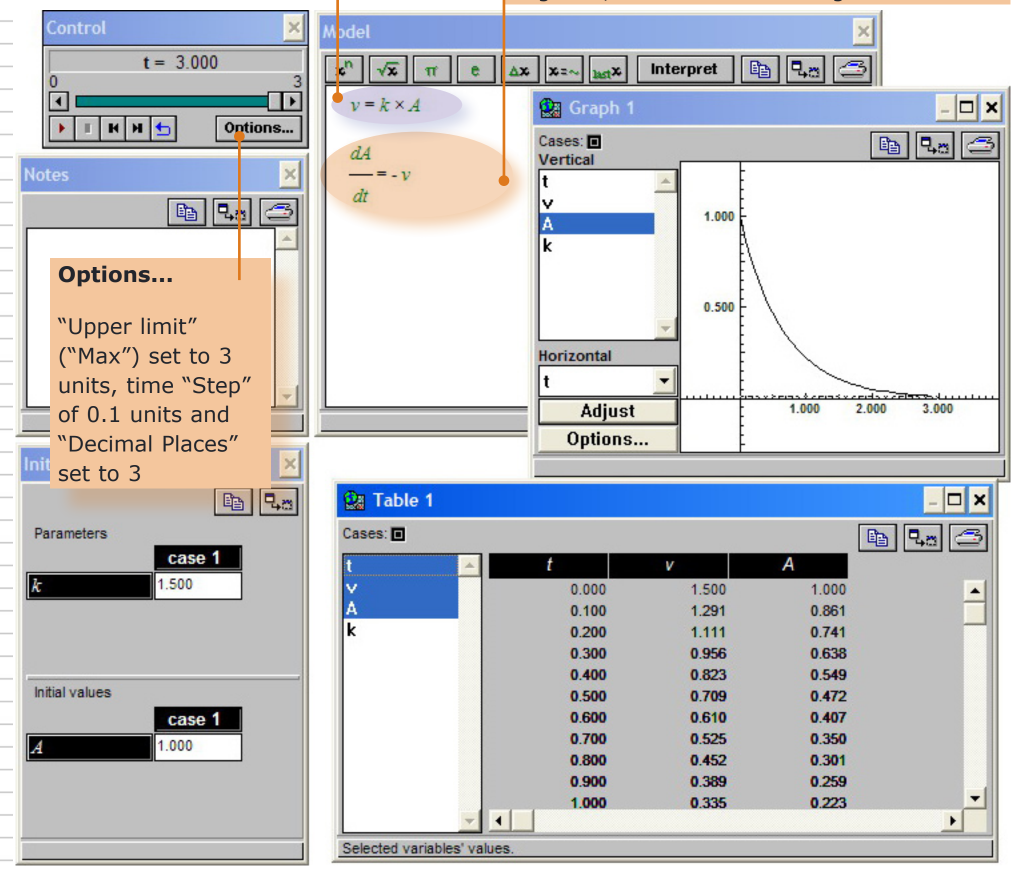
= B10+delta_t

Edit / Fill Down...



The rate law...

The instantaneous rate of change of *A* is negative, since *A* is decreasing at rate *-v*



t	*v*	*A*
0.000	1.500	1.000
0.100	1.291	0.861
0.200	1.111	0.741
0.300	0.956	0.638
0.400	0.823	0.549
0.500	0.709	0.472
0.600	0.610	0.407
0.700	0.525	0.350
0.800	0.452	0.301
0.900	0.389	0.259
1.000	0.335	0.223

Options...

"Upper limit" ("Max") set to 3 units, time "Step" of 0.1 units and "Decimal Places" set to 3

Modelling non-reversible chemical reactions in Modellus

$$v1 = k1 \times A$$

$$\frac{dA}{dt} = -v1$$

$$\frac{dB}{dt} = v1$$

A → B

1. Let's now make minor changes on the Modellus model of the chemical reaction A → B...

2. The reaction has a **rate law** $v_1 = k_1 A$...

3. The concentration of **reactant** A is **decreasing** at a rate v_1...

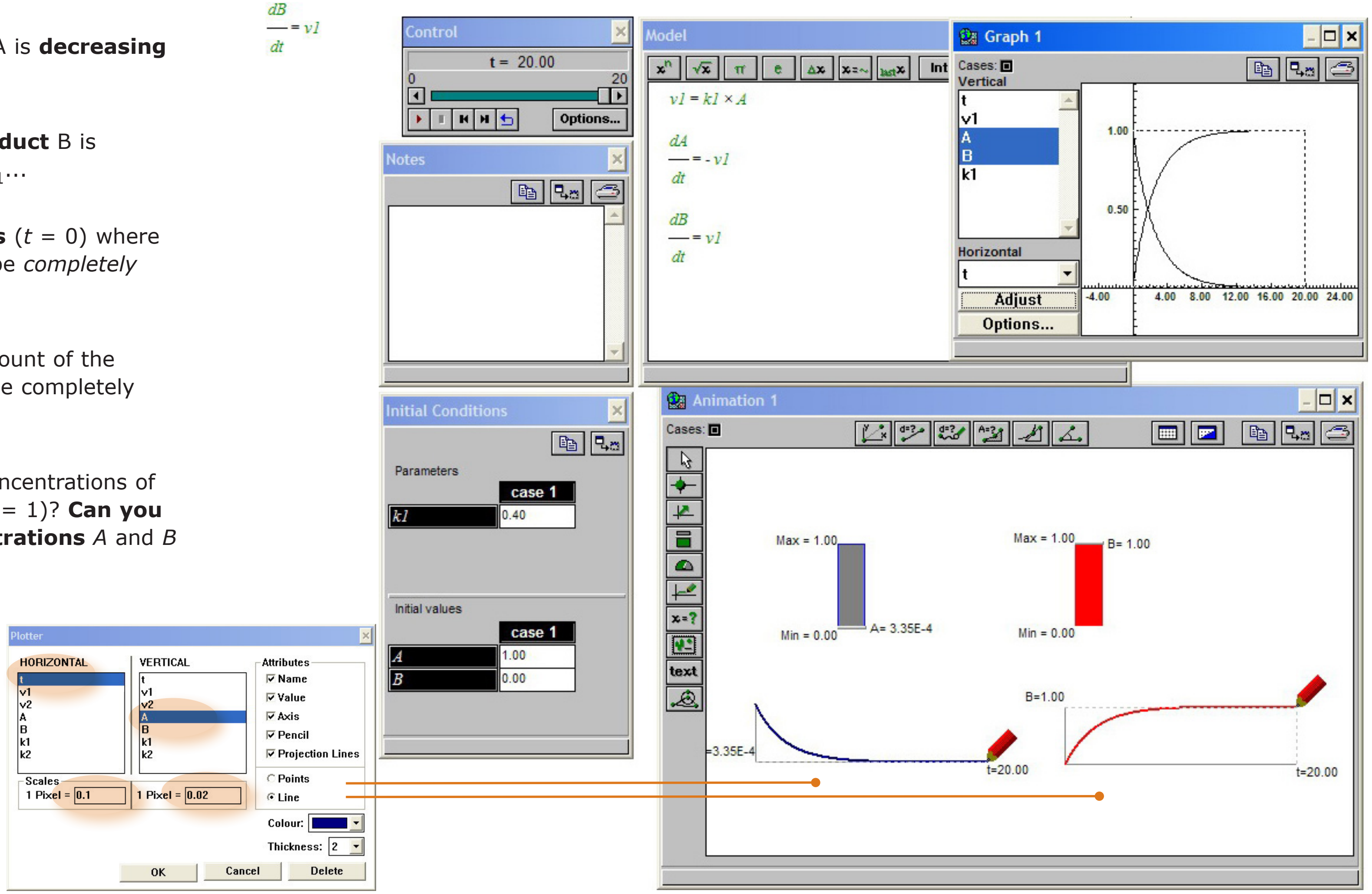
4. ... and the concentration of **product** B is **increasing** at the same rate, v_1...

5. Starting from **initial conditions** (t = 0) where there is *only* reactant A, A will be *completely transformed* into B.

6. If at time t = 0 there is any amount of the product B, reactant A will also be completely transformed into B.

7. What happens if at t = 0 the concentrations of A and B are **equal** (e.g., $A = B = 1$)? **Can you sketch the graphs of concentrations** A and B as functions of time?

8. **Check** you conclusions with the model.



Modelling reversible chemical reactions in Modellus

1. You will now make a model of the simplest **reversible reaction**: $A \rightleftarrows B$, i.e., a reaction where a chemical species A is transformed into a chemical species B, and, at the same time, B is also transformed into A.

2. The **direct** reaction, $A \rightarrow B$, has a **rate law** $v_1 = k_1 A$... and the **inverse** reaction, $B \rightarrow A$, has a **rate law** $v_2 = k_2 B$. (According to the **law of mass action**, the *rate law is proportional to the reactants*. See, e.g., http://en.wikipedia.org/wiki/Law_of_mass_action.)

3. Starting from **initial conditions** ($t = 0$) where there is **only reactant** A, A will be transformed into B and B will also start to be transformed into A... until *both concentrations become constant*. **Equilibrium** is reached after a certain time, that depends on the value of the rate constants, k_1 and k_2. Change the values of these constants to check how they affect the time taken to reach the equilibrium...

4. If at time $t = 0$ **only** species B is present, will the reaction take place? What do you expect to happen to the concentration of the species A?

5. What happens if at $t = 0$ the *concentrations* of A and B are **equal** (e.g., $A = B = 1$) but the *rate constants* are **different**? Can you sketch the graphs of concentrations A and B as functions of time? Check you conclusions with the model.

6. And what happens if the rate constants are equal? Check and discuss...

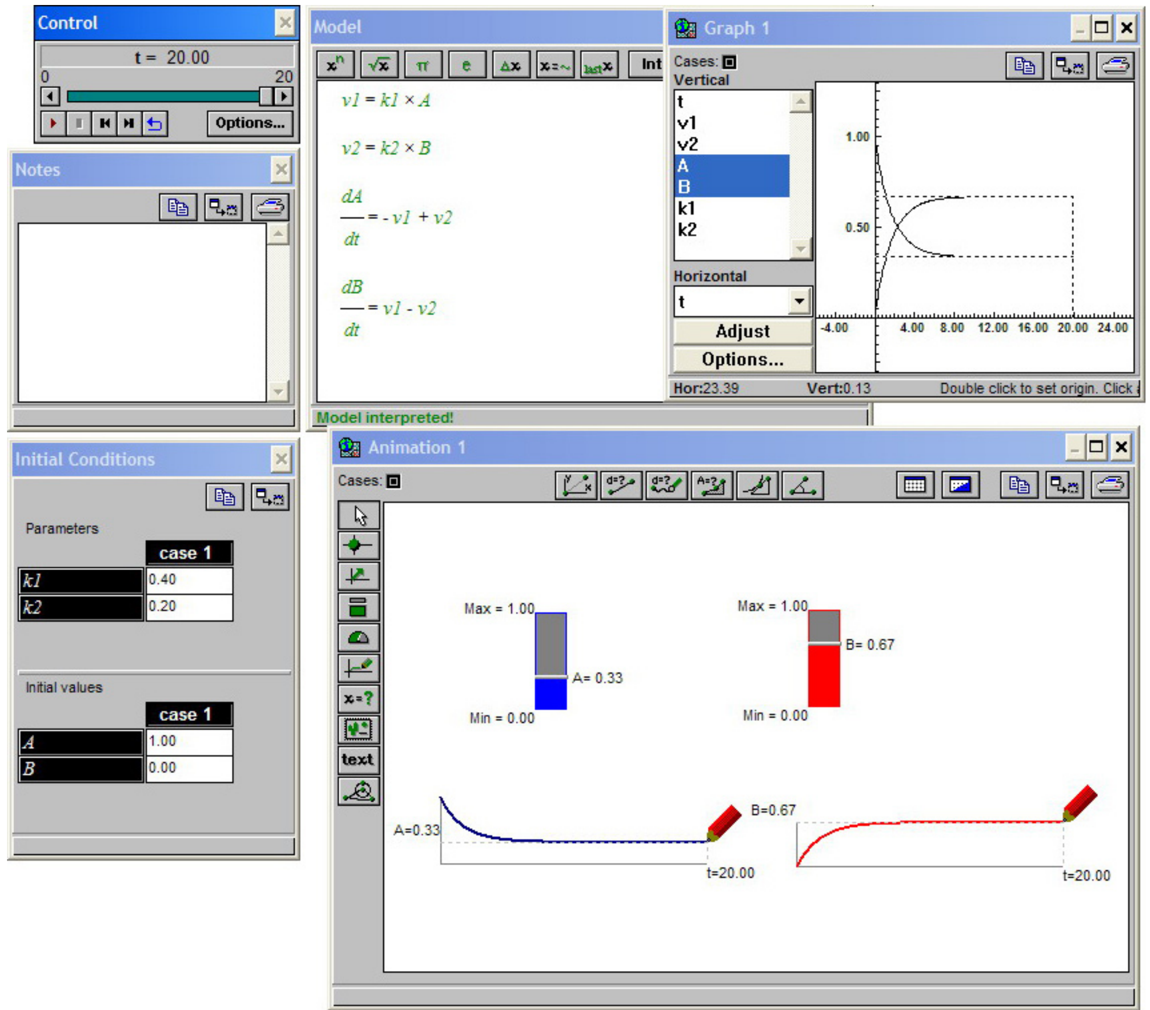
$v1 = k1 \times A$

$v2 = k2 \times B$

$$\frac{dA}{dt} = -v1 + v2$$

$$\frac{dB}{dt} = v1 - v2$$

$$A \rightleftarrows B$$

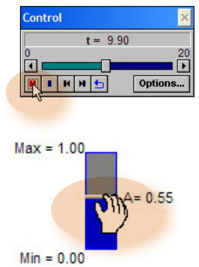


Chemical equilibrium and change in concentration in equilibrium

$$A \rightleftarrows B$$

1. Let's look again the model of the simplest reversible reaction A ⇄ B.

2. Modellus allows the user to *interactively change any independent parameter or any variable* that is changing according to a certain instantaneous rate of change. For example, the user can change the value of the concentration *A* while the model is running.



3. After the system reached equilibrium and while the model is running, press the **Pause button**.

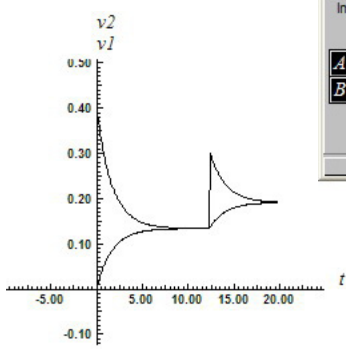
4. Use the mouse to **increase the current value of the concentration** of reactant A...

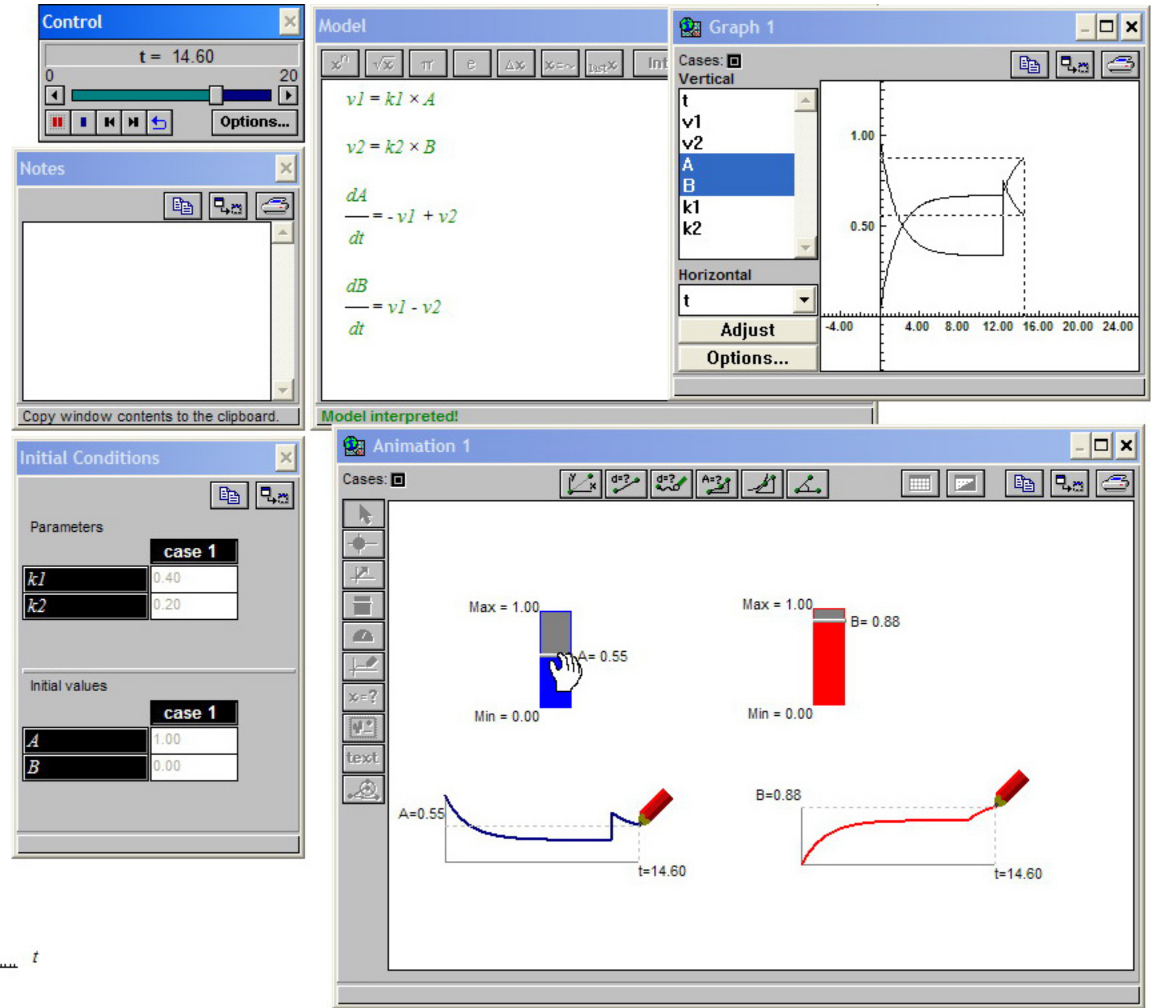
5. Press the Pause button again...

6. **How does the system reacts to this perturbation** to the equilibrium?

7. And how would the system react if the concentration of species B was increased instead of species A?

8. Analyse the **graphs of the velocity** of the direct and inverse reactions (right). Are these graphs *coherent* with the perturbation to the equilibrium? Explain your reasoning. (To learn more about perturbations to chemical equilibrium see, e.g., http://en.wikipedia.org/wiki/Le_Chatelier's_principle.)





Modelling reversible chemical reactions in Modellus, with two "reactants" and one "product"

$$A+B \rightleftarrows C$$

$$v1 = k1 \times A \times B$$

$$v2 = k2 \times C$$

$$\frac{dA}{dt} = -v1 + v2$$

$$\frac{dB}{dt} = -v1 + v2$$

$$\frac{dC}{dt} = v1 - v2$$

1. On the model shown on the right, species A reacts with B to give C, and, at the same time, C is also transformed into A and B.

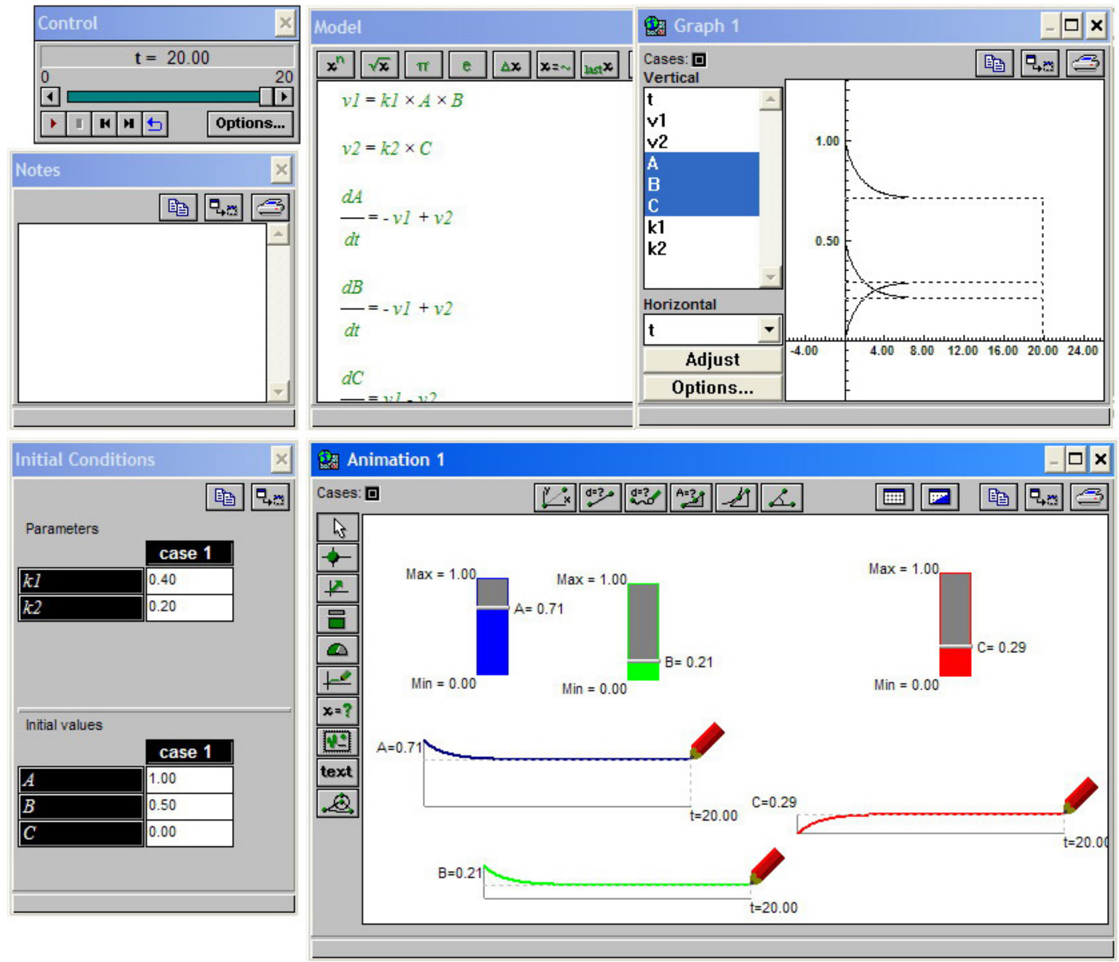
2. The **direct** reaction, $A + B \rightarrow C$, has a **rate law** $v_1 = k_1\ A\ B$ and the **inverse** reaction, $C \rightarrow A + B$, has a **rate law** $v_2 = k_2\ C$.

3. Starting from **initial conditions** (t = 0) where there is **only reactants** A and B, A and B will be transformed into C and C into A and B... until *all concentrations become constant*. **Equilibrium** is reached after a certain time, that depends on the value of the rate constants, k_1 and k_2. Change the values of these constants to check how they affect the time taken to reach the equilibrium...

4. If at time t = 0 **only** species C is present, will the reaction take place? What do you expect to happen to the concentration of the species A and B? Explain your reasoning and check with the model.

5. What happens if at t = 0 the *concentrations* of A, B and C are **equal** (e.g., $A = B = C = 1$) but the *rate constants* are **different**? Can you sketch the graphs of concentrations A, B and C as functions of time? Check you conclusions with the model.

6. And what happens if the rate constants are equal? Check and discuss...



Modelling reversible chemical reactions in Modellus, with one "reactant" and two "products"

$$A \rightleftarrows B + C$$

$$v1 = k1 \times A$$

$$v2 = k2 \times B \times C$$

$$\frac{dA}{dt} = -v1 + v2$$

$$\frac{dB}{dt} = v1 - v2$$

$$\frac{dC}{dt} = v1 - v2$$

1. On the model shown on the right, species A reacts to give B and C, and, at the same time, B and C reacts to give again A.

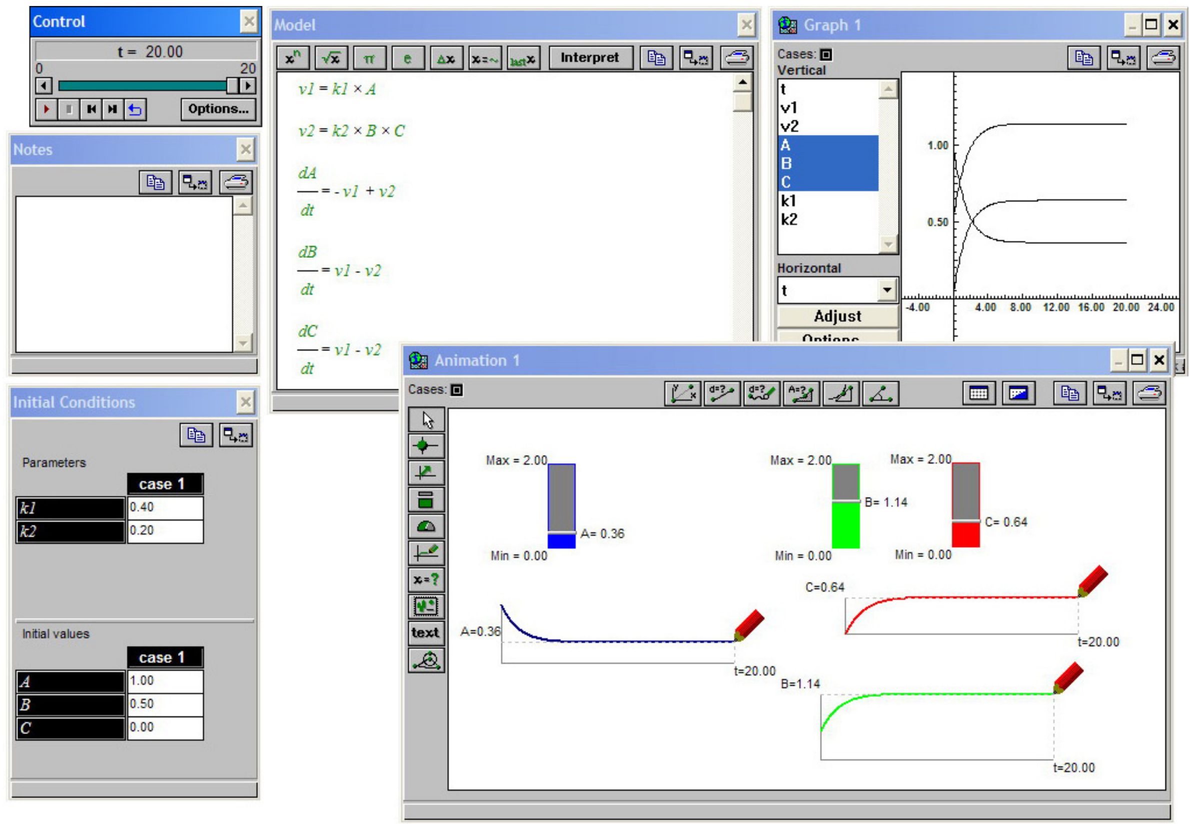
2. The **direct** reaction, $A \rightarrow B + C$, has a **rate law** $v_1 = k_1\,A$ and the **inverse** reaction, $B + C \rightarrow A$, has a **rate law** $v_2 = k_2\,B\,C$.

3. Starting from **initial conditions** ($t = 0$) where there is **only reactant** A, A will be transformed into B and C, and B and C will be transformed into A... until *all concentrations become constant*. **Equilibrium** is reached after a certain time, that depends on the value of the rate constants, k_1 and k_2. Change the values of these constants to check how they affect the time taken to reach the equilibrium...

4. If at time $t = 0$ **only** species A is present, will the reaction take place? What do you expect to happen to the concentration of the species B and C?

5. What happens if at $t = 0$ the *concentrations* of A, B and C are **equal** (e.g., $A = B = C = 1$) but the *rate constants* are **different**? Can you sketch the graphs of concentrations A, B and C as functions of time? Check you conclusions with the model.

6. And what happens if the rate constants are equal? Check and discuss...



Modelling two successive chemical reactions in Modellus, first and second step irreversibles

1. The model shown on the right represents two successive reactions: species A reacts to give B, and B reacts to give C.

2. The **first** reaction, A → B, has a **rate law** $v_1 = k_1\,A$ and the **second** reaction, B → C, has a **rate law** $v_2 = k_2\,B$.

3. The concentration of species A is **decreasing** at a rate v_1...

4. ... and the concentration of species B is **increasing** at a rate v_1 (receiving from A) and **decreasing** at a rate v_2 (forming C)...

5. ... and the concentration of species C is **increasing** at a rate v_2 (receiving from B)...

6. Starting from **initial conditions** (t = 0) where there is *only* reactant A, A will be *completely transformed* into B and B into C...

7. What happens if at t = 0 there is any amount of the species A and B but no C? Discuss, explain your reasoning, predict and check.

8. What happens if at t = 0 there is any amount of the species B but no A and C? Discuss, explain your reasoning, predict and check.

9. What happens if at t = 0 there is any amount of the species A and reaction 1 occurs at a "high" rate and reaction 2 at a "low" rate (e.g., k_1 = 1.0 and k_2 = 0.1)? Discuss, explain your reasoning, predict and check.

$$v1 = k1 \times A$$

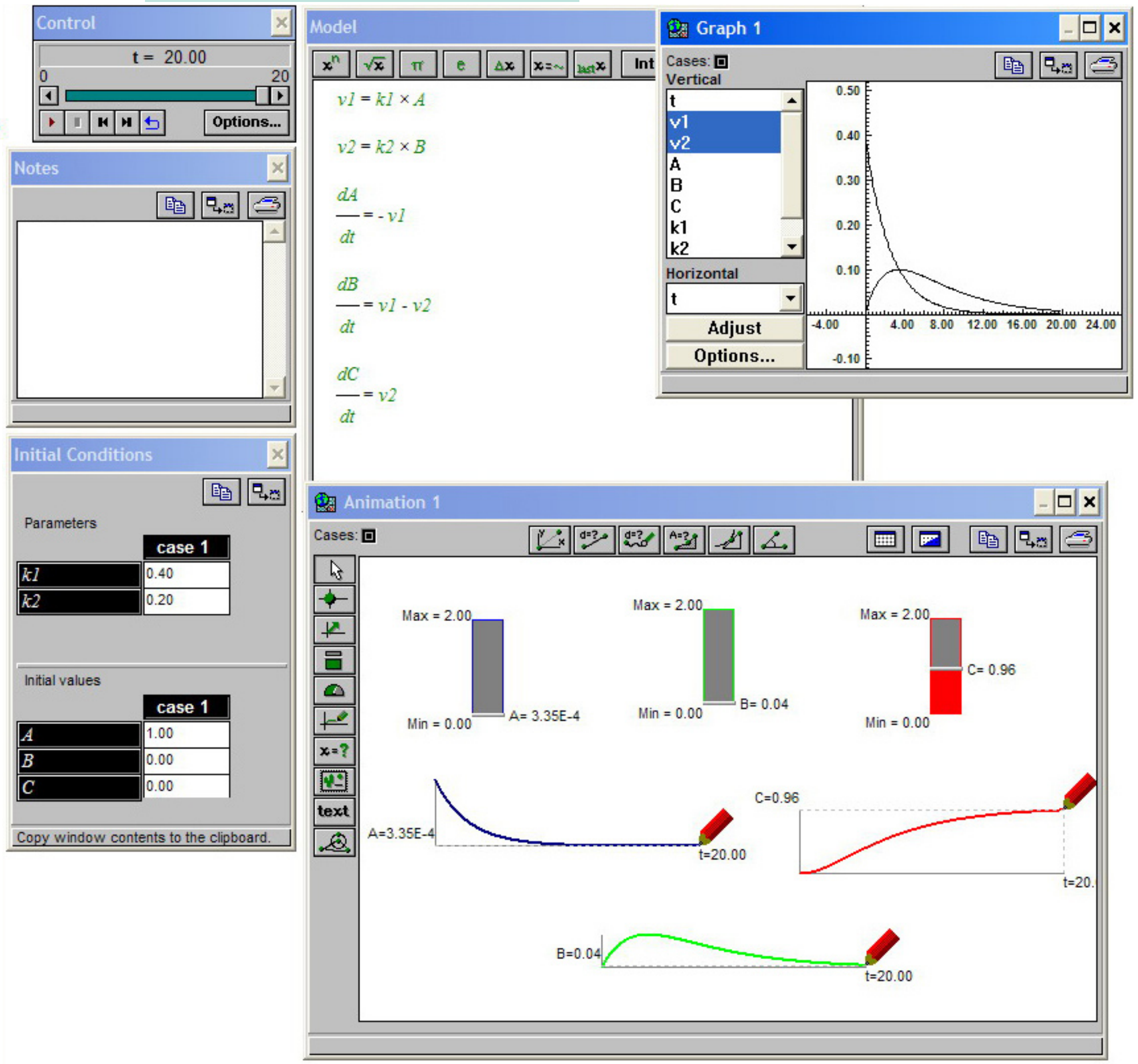
$$v2 = k2 \times B$$

$$\frac{dA}{dt} = -v1$$

$$\frac{dB}{dt} = v1 - v2$$

$$\frac{dC}{dt} = v2$$

A → B → C



Modelling successive chemical reactions in Modellus, first step reversible, second irreversible...

$$A \rightleftarrows B \rightarrow C$$

1. The model shown on the right represents successive reactions: species A reacts **reversibly** to give B and B reacts **irreversibly** to give C.

2. The concentration of species A is **decreasing** at a rate v_1 (reaction A → B) and **increasing** at a rate v_2 (reaction B → A)...

3. ... and the concentration of species B is **increasing** at a rate v_1 (receiving from A) and **decreasing** at a rate v_2 (forming A) but **also decreasing** at a rate v_3 (forming C, reaction B → C)...

4. ... and the concentration of species C is **increasing** at a rate v_3 (receiving from B, reaction B → C).

5. What happens if at t = 0 there is any amount of the species A and B but no C? Discuss, explain your reasoning, predict and check.

6. What happens if at t = 0 there is any amount of the species B but no A and C? Discuss, explain your reasoning, predict and check.

7. What happens if at t = 0 there is any amount of the species C but no A and B? Discuss, explain your reasoning, predict and check.

$$v1 = k1 \times A$$

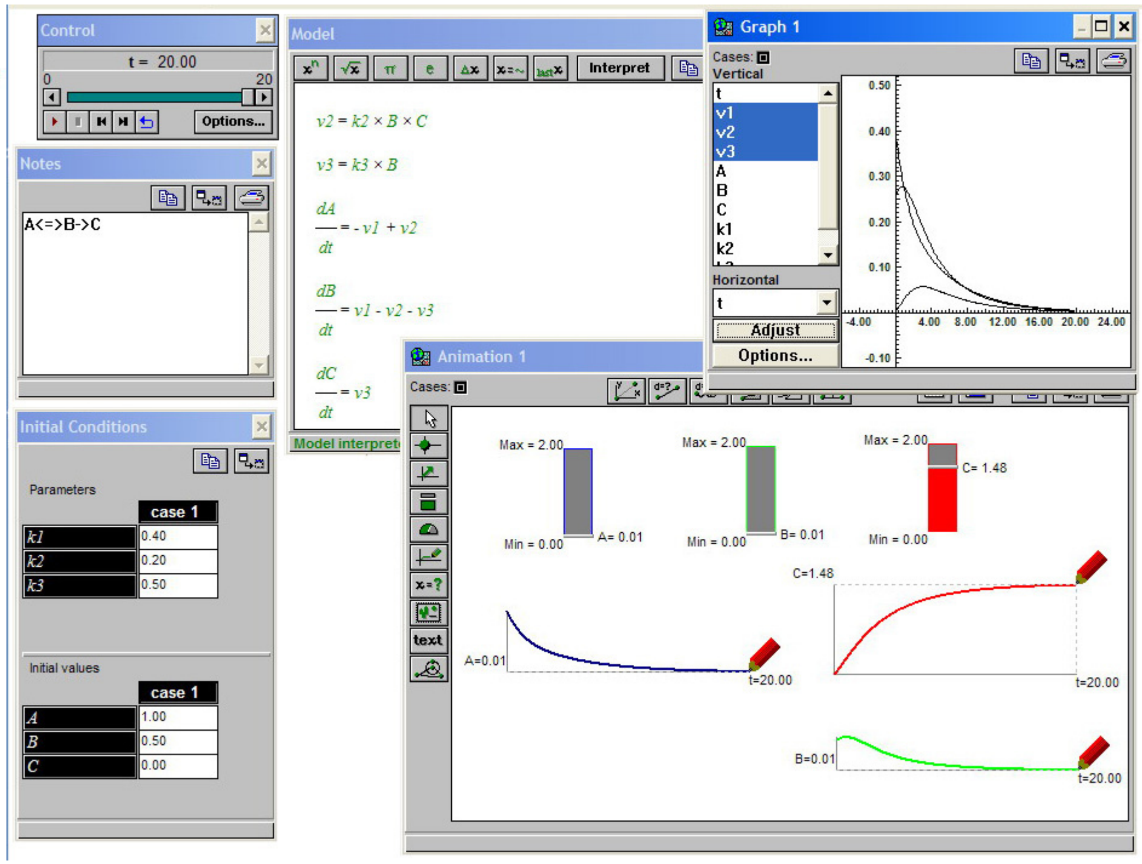
$$v2 = k2 \times B$$

$$v3 = k3 \times B$$

$$\frac{dA}{dt} = -v1 + v2$$

$$\frac{dB}{dt} = v1 - v2 - v3$$

$$\frac{dC}{dt} = v3$$



Modelling successive chemical reactions in Modellus, first step irreversible, second reversible...

$$A \rightarrow B \rightleftarrows C$$

1. The model shown on the right represents successive reactions: species A reacts **irreversibly** to give B and B reacts **reversibly** to give C.

2. The concentration of species A is **decreasing** at a rate v_1 (reaction $A \rightarrow B$)...

3. ... and the concentration of species B is **increasing** at a rate v_1 (receiving from A), **decreasing** at a rate v_2 (forming C, reaction $B \rightarrow C$) but **also increasing** at a rate v_3 (receiving from C, reaction $C \rightarrow B$)...

4. ... and the concentration of species C is **increasing** at a rate v_2 (receiving from B, reaction $B \rightarrow C$) and **decreasing** at a rate v_3 (forming B, reaction $C \rightarrow B$).

5. What happens if at t = 0 there is any amount of the species A and B but no C? Discuss, explain your reasoning, predict and check.

6. What happens if at t = 0 there is any amount of the species B but no A and C? Discuss, explain your reasoning, predict and check.

7. What happens if at t = 0 there is any amount of the species C but no A and B? Discuss, explain your reasoning, predict and check.

$$v1 = k1 \times A$$

$$v2 = k2 \times B$$

$$v3 = k3 \times C$$

$$\frac{dA}{dt} = -v1$$

$$\frac{dB}{dt} = v1 - v2 + v3$$

$$\frac{dC}{dt} = v2 - v3$$