To parallelle 1. hhv. 2. ordens reaktioner

http://en.wikipedia.org/wiki/Rate_law#Parallel_or_competitive_reactions

$A \to B$ og $A \to C$

2 parallelle **1.** hhv. **2. ordens** reaktioner med reaktionskonstanterne k_B og k_C.

Differentialligningssystem:

$$\frac{d[A]}{dt} = -k_B \cdot [A] - k_C \cdot [A]^2$$

$$\frac{d[B]}{dt} = k_B \cdot [A]$$

$$\frac{d[C]}{dt} = k_C \cdot [A]^2$$

Differentialligningssystemet løst direkte med Maple

```
> restart
```

Differentialligninger:

```
> DL1 := A'(t) = -k_B·A(t) - k_C·A(t)^2;
  DL2 := B'(t) = k_B·A(t);
  DL3 := C'(t) = k_C·A(t)^2
```

$$DL1 := \mathrm{D}(A)(t) = -k_B A(t) - k_C A(t)^2$$

$$DL2 := \mathrm{D}(B)(t) = k_B A(t)$$

$$DL3 := \mathrm{D}(C)(t) = k_C A(t)^2 \qquad \textbf{(1.1)}$$

Startbetingelser:

```
> BT1 := A(0) = A_0;
  BT2 := B(0) = 0;
  BT3 := C(0) = 0
```

$$BT1 := A(0) = A_0$$

$$BT2 := B(0) = 0$$

$$BT3 := C(0) = 0 \qquad \textbf{(1.2)}$$

Differentialligningssystemet løses:

```
> dsolve({DL1, DL2, DL3 , BT1, BT2, BT3}, {A(t), B(t), C(t)})
```

(1.3)

$$\left\{A(t) = \frac{k_B}{\frac{e^{k_B t}(A_0 k_C + k_B)}{A_0} - k_C}, B(t) = \frac{k_B \ln\left(\frac{e^{k_B t}(A_0 k_C + k_B)}{A_0} - k_C\right)}{k_C} - \frac{k_B \ln\left(e^{k_B t}\right)}{k_C} - \frac{k_B \ln\left(\frac{k_B}{A_0}\right)}{k_C}, C(t) = -\frac{k_B}{\frac{e^{k_B t}(A_0 k_C + k_B)}{A_0} - k_C} - \frac{k_B \ln\left(\frac{e^{k_B t}(A_0 k_C + k_B)}{A_0} - k_C\right)}{k_C} + \frac{k_B \ln\left(e^{k_B t}\right)}{k_C} + \frac{A_0 k_C + k_B \ln\left(\frac{k_B}{A_0}\right)}{k_C}\right\} \quad \textbf{(1.3)}$$

Løsningerne indlægges i funktioner:

```
> A := unapply(rhs((1.3)[1]), t) :
  B := unapply(rhs((1.3)[2]), t) :
  C := unapply(rhs((1.3)[3]), t) :
```

Løsningerne er:

```
> 'A(t)'=A(t);
  'B(t)'=B(t);
  'C(t)'=C(t)
```

$$A(t) = \frac{k_B}{\frac{e^{k_B t}(A_0 k_C + k_B)}{A_0} - k_C}$$

$$B(t) = \frac{k_B \ln\left(\frac{e^{k_B t}(A_0 k_C + k_B)}{A_0} - k_C\right)}{k_C} - \frac{k_B \ln\left(e^{k_B t}\right)}{k_C} - \frac{k_B \ln\left(\frac{k_B}{A_0}\right)}{k_C}$$

$$C(t) = -\frac{k_B}{\frac{e^{k_B t}(A_0 k_C + k_B)}{A_0} - k_C} - \frac{k_B \ln\left(\frac{e^{k_B t}(A_0 k_C + k_B)}{A_0} - k_C\right)}{k_C} + \frac{k_B \ln\left(e^{k_B t}\right)}{k_C} + \frac{A_0 k_C + k_B \ln\left(\frac{k_B}{A_0}\right)}{k_C} \quad \textbf{(1.4)}$$

Grænseværdierne af koncentrationerne for $t \to \infty$ er:

```
> assume(k_B > 0, k_C > 0); interface(showassumed = 0) :
> 'Grænseværdi af A(t)' = lim(t -> infinity) A(t);
  'Grænseværdi af B(t)' = lim(t -> infinity) B(t);
  'Grænseværdi af C(t)' = lim(t -> infinity) C(t)
```

$$\text{Grænseværdi af } A(t) = 0$$

$$\text{Grænseværdi af } B(t) = \frac{k_B \ln\left(\frac{A_0 k_C + k_B}{A_0}\right) - k_B \ln(k_B) - k_B \ln\left(\frac{1}{A_0}\right)}{k_C}$$

$$\text{Grænseværdi af } C(t) = \frac{A_0 k_C - k_B \ln\left(\frac{A_0 k_C + k_B}{A_0}\right) + k_B \ln(k_B) + k_B \ln\left(\frac{1}{A_0}\right)}{k_C} \qquad \textbf{(1.5)}$$

Eksempel

```
> k_B := 0.3; k_C := 0.1; A_0 := 1
```

$$k_B := 0.3$$
$$k_C := 0.1$$
$$A_0 := 1 \qquad \textbf{(1.1.1)}$$

```
> 'A(t)' = A(t);
  'B(t)' = B(t);
  'C(t)' = C(t)
```

$$A(t) = \frac{0.3}{0.4\, e^{0.3\, t} - 0.1}$$

$$B(t) = 3.000000000 \ln(0.4\, e^{0.3\, t} - 0.1) - 3.000000000 \ln(e^{0.3\, t}) + 3.611918412$$

$$C(t) = -\frac{0.3}{0.4\, e^{0.3\, t} - 0.1} - 3.000000000 \ln(0.4\, e^{0.3\, t} - 0.1) + 3.000000000 \ln(e^{0.3\, t}) - 2.611918412 \qquad \textbf{(1.1.2)}$$

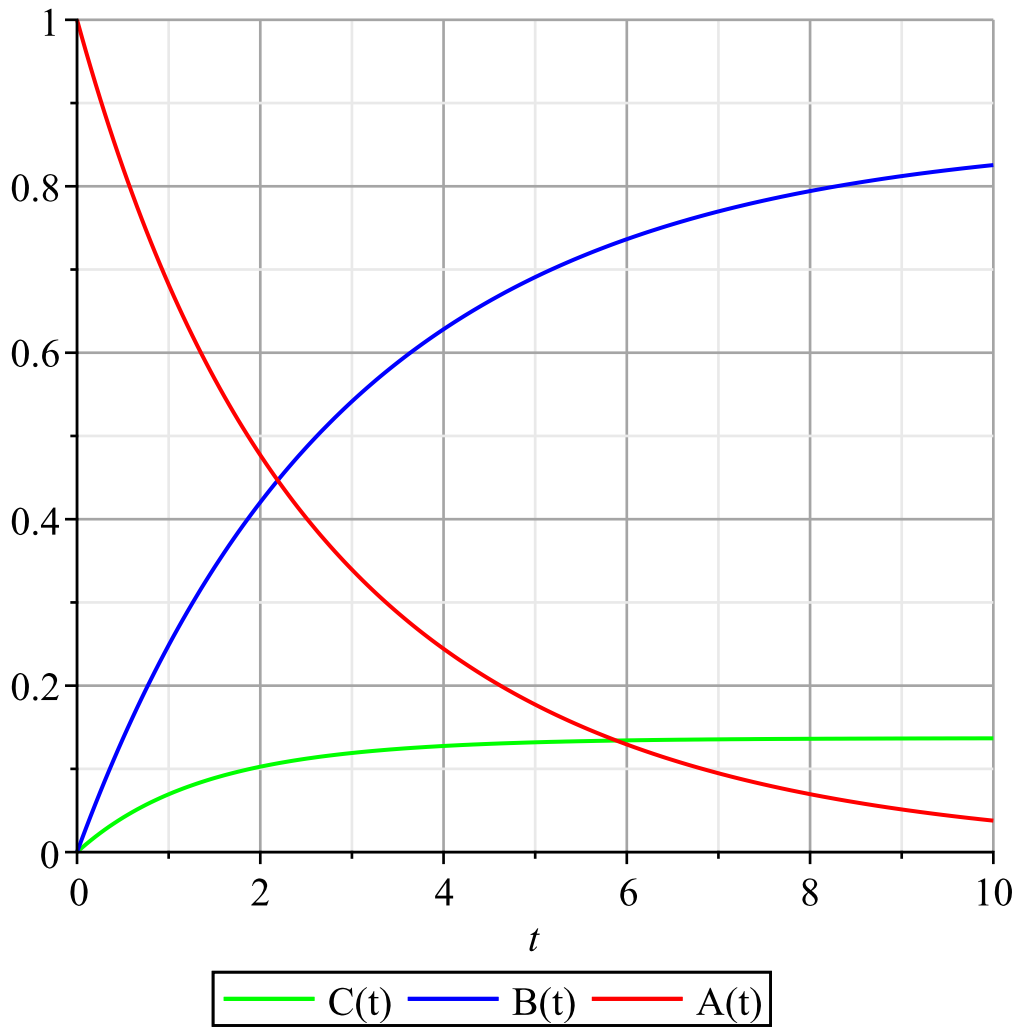
Grænseværdier:

```
> 'Grænseværdi af A(t)' = lim(t -> infinity) A(t);
  'Grænseværdi af B(t)' = lim(t -> infinity) B(t);
  'Grænseværdi af C(t)' = lim(t -> infinity) C(t)
```

$$\text{Grænseværdi af } A(t) = 0.$$
$$\text{Grænseværdi af } B(t) = 0.863046218$$
$$\text{Grænseværdi af } C(t) = 0.136953782 \qquad \textbf{(1.1.3)}$$

```
> pA := plot(A(t), t = 0..10, color = red, gridlines, legend = ["A(t)"]) :
  pB := plot(B(t), t = 0..10, color = blue, gridlines, legend = ["B(t)"]) :
  pC := plot(C(t), t = 0..10, color = green, gridlines, legend = ["C(t)"]) :

> with(plots) :
> display({pA, pB, pC}, gridlines)
```



Successiv løsning med Maple

Differentialligningssystemet kan løses én ligning ad gangen.

```
> restart
```

Differentialligning 1:

```
> DL1 := A'(t) = -k_B·A(t) - k_C·A(t)^2
```

$$DL1 := \mathrm{D}(A)(t) = -k_B A(t) - k_C A(t)^2 \qquad (2.1)$$

Startbetingelse 1:

```
> BT1 := A(0) = A_0
```

$$BT1 := A(0) = A_0 \qquad (2.2)$$

Differentialligning 1 løses:

```
> dsolve({DL1, BT1}, {A(t)})
```

$$A(t) = \frac{k_B A_0}{A_0 \mathrm{e}^{k_B t} k_C - A_0 k_C + \mathrm{e}^{k_B t} k_B} \qquad (2.3)$$

Indlægges i en funktion:

```
> A := unapply(rhs(%), t)
```

$$A := t \mapsto \frac{k_B A_0}{A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B} \tag{2.4}$$

Differentialligning 2:

> $DL2 := B'(t) = k_B \cdot A(t)$

$$DL2 := D(B)(t) = \frac{k_B^2 A_0}{A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B} \tag{2.5}$$

Startbetingelse 2:

> $BT2 := B(0) = 0$

$$BT2 := B(0) = 0 \tag{2.6}$$

Differentialligning 2 løses:

> $dsolve(\{DL2, BT2\}, \{B(t)\})$

$$B(t) = -\frac{k_B \ln\left(e^{k_B t}\right)}{k_C} + \frac{k_B \ln\left(A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B\right)}{k_C} - \frac{k_B \ln(k_B)}{k_C} \tag{2.7}$$

Indlægges i en funktion:

> $B := unapply(rhs(\%), t)$

$$B := t \mapsto -\frac{k_B \ln\left(e^{k_B t}\right)}{k_C} + \frac{k_B \ln\left(A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B\right)}{k_C} - \frac{k_B \ln(k_B)}{k_C} \tag{2.8}$$

Differentialligning 3:

> $DL3 := C'(t) = k_C \cdot A(t)^2$

$$DL3 := D(C)(t) = \frac{k_C k_B^2 A_0^2}{\left(A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B\right)^2} \tag{2.9}$$

Startbetingelse 3:

> $BT3 := C(0) = 0$

$$BT3 := C(0) = 0 \tag{2.10}$$

Differentialligning 3 løses:

> $dsolve(\{DL3, BT3\}, \{C(t)\})$

$$C(t) = \frac{k_B \ln\left(e^{k_B t}\right)}{k_C} - \frac{k_B A_0}{A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B} \tag{2.11}$$
$$- \frac{k_B A_0 \ln\left(A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B\right)}{A_0 k_C + k_B} - \frac{k_B^2 \ln\left(A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B\right)}{k_C \left(A_0 k_C + k_B\right)}$$
$$+ A_0 + \frac{k_B A_0 \ln(k_B)}{A_0 k_C + k_B} + \frac{k_B^2 \ln(k_B)}{k_C \left(A_0 k_C + k_B\right)}$$

Indlægges i en funktion:

> $C := unapply(rhs(\%), t)$

(2.12)

$$C := t \mapsto \frac{k_B \ln\left(e^{k_B t}\right)}{k_C} - \frac{k_B A_0}{A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B} \tag{2.12}$$
$$- \frac{k_B A_0 \ln\left(A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B\right)}{A_0 k_C + k_B} - \frac{k_B^2 \ln\left(A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B\right)}{k_C \left(A_0 k_C + k_B\right)}$$
$$+ A_0 + \frac{k_B A_0 \ln(k_B)}{A_0 k_C + k_B} + \frac{k_B^2 \ln(k_B)}{k_C \left(A_0 k_C + k_B\right)}$$

Løsningerne:

```
> 'A(t)'=A(t);
  'B(t)'=B(t);
  'C(t)'=C(t)
```

$$A(t) = \frac{k_B A_0}{A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B}$$

$$B(t) = -\frac{k_B \ln\left(e^{k_B t}\right)}{k_C} + \frac{k_B \ln\left(A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B\right)}{k_C} - \frac{k_B \ln(k_B)}{k_C}$$

$$C(t) = \frac{k_B \ln\left(e^{k_B t}\right)}{k_C} - \frac{k_B A_0}{A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B} \tag{2.13}$$
$$- \frac{k_B A_0 \ln\left(A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B\right)}{A_0 k_C + k_B} - \frac{k_B^2 \ln\left(A_0 e^{k_B t} k_C - A_0 k_C + e^{k_B t} k_B\right)}{k_C \left(A_0 k_C + k_B\right)}$$
$$+ A_0 + \frac{k_B A_0 \ln(k_B)}{A_0 k_C + k_B} + \frac{k_B^2 \ln(k_B)}{k_C \left(A_0 k_C + k_B\right)}$$

Umuligt at se, om $B(t)$ er samme løsning som før?

Løsning med håndkraft

1. differentialligning:

Kan omskrives til: $A'(t) = -k_B \cdot A(t) - k_C \cdot (A(t))^2 \Leftrightarrow A'(t) = A(t) \cdot \left(-k_B - k_C \cdot A(t)\right)$

Dette er en **logistisk differentialligning** (sætning 13a i A-bogen) med: $a = k_C$ og $b = -k_B$.

Normalt forudsætter vi, at a og b er positive tal. Mne løsningen er alligevel OK:

$$A(t) = \frac{\frac{b}{a}}{1 + c \cdot e^{-b \cdot t}} \text{ dvs. } A(t) = \frac{\frac{-k_B}{k_C}}{1 + c \cdot e^{k_B \cdot t}}$$

Her skal $A(0) = A_0$,

dvs.

$$A_0 = \frac{\frac{-k_B}{k_C}}{1 + c \cdot e^{k_B \cdot 0}} \Leftrightarrow A_0 = \frac{\frac{-k_B}{k_C}}{1 + c} \Leftrightarrow 1 + c = \frac{\frac{-k_B}{k_C}}{A_0} \Leftrightarrow 1 + c = -\frac{k_B}{k_C \cdot A_0} \Leftrightarrow c = -1 - \frac{k_B}{k_C \cdot A_0}$$

$$A(t) = \frac{\frac{-k_B}{k_C}}{1 + \left(-1 - \frac{k_B}{k_C \cdot A_0}\right) \cdot e^{k_B \cdot t}} \Leftrightarrow \boldsymbol{A(t) = \frac{\frac{k_B}{k_C}}{\left(1 + \frac{k_B}{k_C \cdot A_0}\right) \cdot e^{k_B \cdot t} - 1}}$$

2. differentialligning:

Kan nu løses ved indsætning og derefter 'bare' **integration**!

3. differentialligning:

Kan nu løses ved indsætning og derefter 'bare' **integration**!

Er det samme løsning som Maple giver?