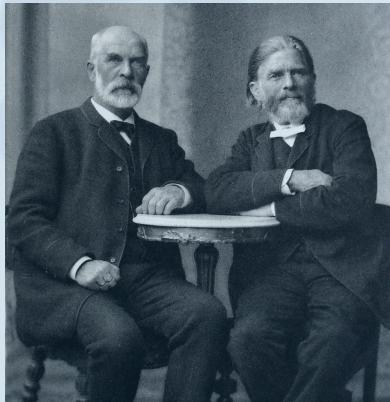


## Digression on (**mesoscopic**) (chemical) reactions (i.e., alias kinetic schemes): population descriptions!



Cato Maximilian **Guldberg**  
Peter **Waage**, (Norway) 1865

### The Mass Action Law

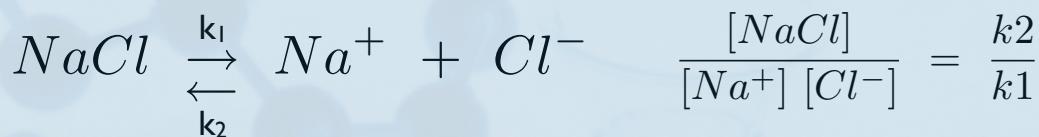
*if A reacts with B to form substance C,  
then the rate of production of C is  
proportional to the amount of A & B*



$$\begin{aligned} \text{Rate of Prod. of } C &= \\ &= k [A] [B] \end{aligned}$$

It follows from first principles of equilibrium thermodynamics.

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$$[Na^+] = ??? \frac{\text{moles}}{\text{litre}}$$

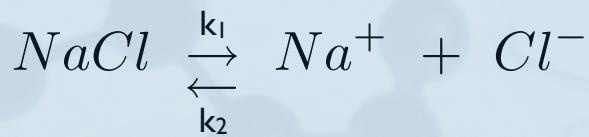
Avogadro's number  
1 mole =  $6.022 \times 10^{23}$  molecules  
1 litre = 1 dm<sup>3</sup> = 1000 cm<sup>3</sup>



$$vol\ [Na^+] = ??? \text{ moles} = ??????? \text{ molecules}$$

A chemical reaction describes when (the density, or concentration of)  
“something” is *transformed* into “something else” (or gets another “form”).

## Kinetic scheme is equivalent to a (system of) o.d.e.!



$$\frac{d[NaCl]}{dt} = -k_1[NaCl] + k_2[Na^+][Cl^-]$$

at steady-state...  $0 = -k_1[NaCl] + k_2[Na^+][Cl^-]$

rearranging the terms proves the relationship:

$$\frac{[NaCl]}{[Na^+] [Cl^-]} = \frac{k_2}{k_1}$$

$$A \xrightarrow{k} C$$

$$\frac{d}{dt}[A] = -k [A]$$

$$\frac{d}{dt}[C] = k [A]$$

$$[A] + [C] = \text{fixed}$$

$$A \xrightleftharpoons[k_2]{k_1} C$$

$$\frac{d}{dt}[A] = -k_1 [A] + k_2 [C]$$

$$\frac{d}{dt}[C] = k_1 [A] - k_2 [C]$$

$$[A] + [C] = \text{fixed}$$

$$A + B \xrightarrow{k} C$$

$$\frac{d}{dt}[A] = -k [A][B]$$

$$\frac{d}{dt}[B] = -k [A][B]$$

$$\frac{d}{dt}[C] = k [A][B]$$

$$[A] + [B] + 2[C] = \text{fixed}$$

$$A + B \xrightleftharpoons[k_2]{k_1} C$$

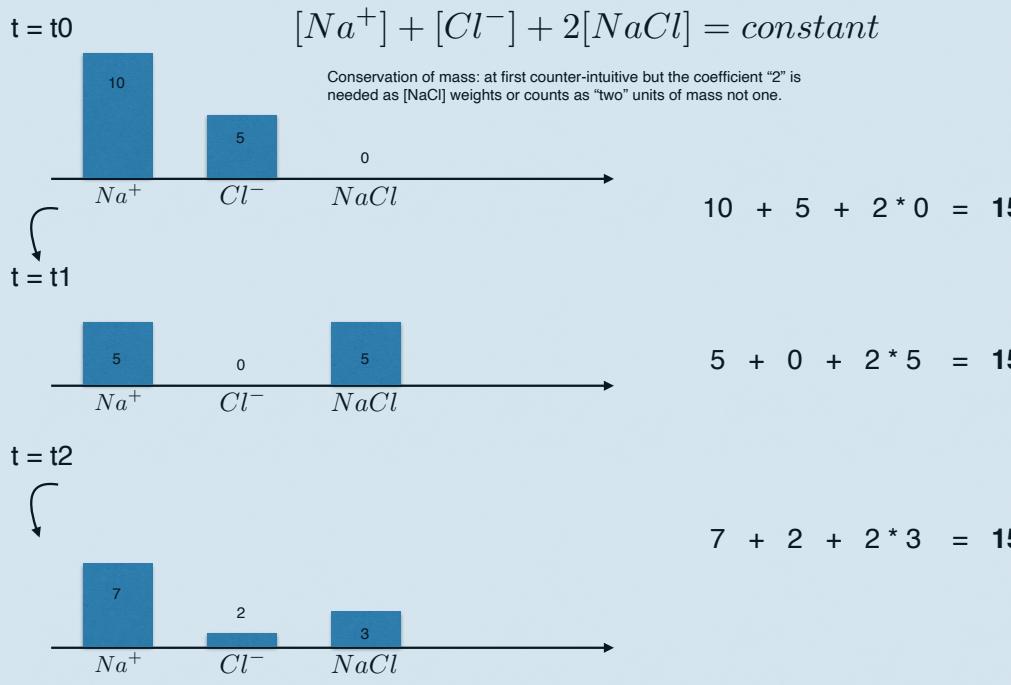
$$\frac{d}{dt}[A] = -k_1 [A][B] + k_2 [C]$$

$$\frac{d}{dt}[B] = -k_1 [A][B] + k_2 [C]$$

$$\frac{d}{dt}[C] = k_1 [A][B] - k_2 [C]$$

$$[A] + [B] + 2[C] = \text{fixed}$$

## Conservation of mass: in agreement with our intuition



$$\frac{1}{n} \frac{d}{dt}[A] = -k_1 [A]^n[B]$$

$$\frac{d}{dt}[B] = -k_1 [A]^n[B]$$

$$\frac{d}{dt}[C] = k_1 [A]^n[B]$$

$$[A] + [B] + (n+1)[C] = \text{fixed}$$



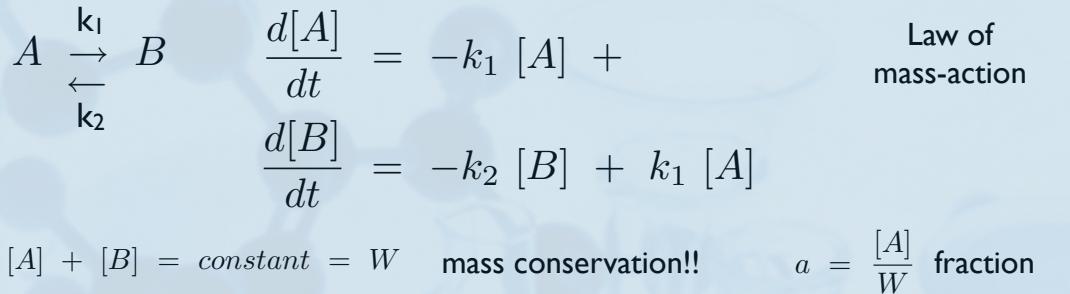
$$\frac{1}{n} \frac{d}{dt}[A] = -k_1 [A]^n[B] + k_2 [C]$$

$$\frac{d}{dt}[B] = -k_1 [A]^n[B] + k_2 [C]$$

$$\frac{d}{dt}[C] = k_1 [A]^n[B] + -k_2 [C]$$

$$[A] + [B] + (n+1)[C] = \text{fixed}$$

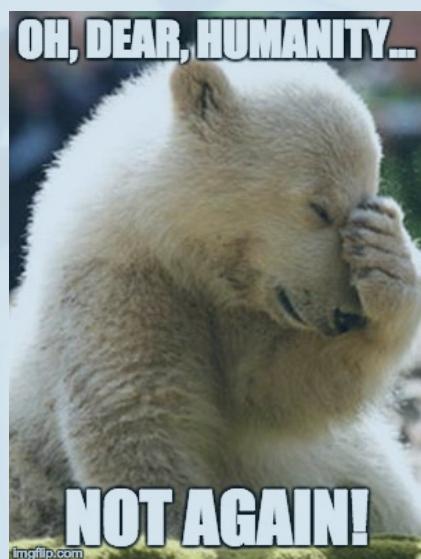
## Digression on (**mesoscopic**) (chemical) reactions (i.e., alias kinetic schemes): population descriptions!



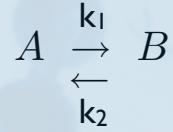
$$\frac{da}{dt} = -k_1 a + k_2 (1 - a) \quad \frac{da}{dt} = -(k_1 + k_2) a + k_2$$

The *reactions* are described at the ensemble level as first-order kinetics phenomena: they depend only on the concentration of the “reactants”.

$$\frac{da}{dt} = -(k_1 + k_2) a + k_2$$



## What about a microscopic, i.e., single-molecule description?



$$Pr\{A \rightarrow B \text{ in } (t ; t + \Delta t] / \text{state } A \text{ at } t\} = k_1 \Delta t + O(\Delta t)$$

$$Pr\{B \rightarrow A \text{ in } (t ; t + \Delta t] / \text{state } B \text{ at } t\} = k_2 \Delta t + O(\Delta t)$$

$$Pr\{> \text{ one transition in } (t ; t + \Delta t]\} \approx 0$$

$$Pr = f(\Delta t) \approx = 0 + k \Delta t + \dots$$

Same notation, but different meaning:  
NOT concentrations/densities, but occupancy probabilities.