

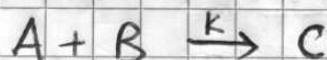
A/6/10

Math 250B

[ref. 'A Course in Mathematical Biology', SIAM]

Goal: To look at a practical example where autonomous systems of first order ODEs are very useful. In particular, we will look at the LAW OF MASS ACTION and its implications in chemistry for reversible reactions and Michaelis-Menten kinetics

starting point: Consider an irreversible reaction where two reactants (A and B) combine to produce C [A and B are commonly referred to as the reactants while C is called the product]



where k (commonly referred to as the reaction constant) essentially specifies the rate at which A and B interact to produce C

□ one way to conceptualize this rate equation:

$$\left[\begin{array}{c} \# \text{ of collisions of} \\ \text{molecules A and B} \end{array} \right] \left[\begin{array}{c} \text{probability that a collision has} \\ \text{enough energy to initiate a reaction} \end{array} \right] = \left[\begin{array}{c} \text{change of the product} \\ \text{over some time} \end{array} \right]$$

□ Introduce some new variables:

$$\left. \begin{array}{l} a \equiv [A] \\ b \equiv [B] \\ c \equiv [C] \end{array} \right\} \begin{array}{l} \text{concentrations (say, } \frac{\text{mol}}{\text{L}} \text{) of} \\ \text{the various participants} \end{array}$$

let $r_1 \approx$ probability of a collision of A and B

$r_2 \approx$ probability that a given collision has enough energy to overcome the activation energy required for a reaction

- then $r_1 a b \Delta t$ is a good approximation as to the # of collisions that occur over some time interval Δt
- factoring in the probability r_2 and letting ΔC denote the change of the product C over some time interval (say, Δt), then we have

$$\Delta C \approx r_2 (r_1 a b \Delta t) = k a b \Delta t$$

where $k \equiv r_1 r_2$ (this is the reaction constant!)
(taking the volumes of things into account...)

thus $\frac{\Delta C}{\Delta t} \approx k a b$, so taking the limit $\Delta t \rightarrow 0$

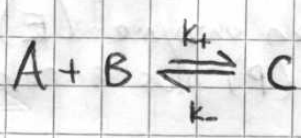
$$\Rightarrow \left[\frac{dC}{dt} = k a b \right]$$

LAW OF MASS ACTION (LMA)

- so, essentially, the LMA is just a first-order ODE
- keep in mind that we were somewhat cavalier in deriving it and thus it is really only an approximation (sometimes a very good one!); for example, the validity of the LMA is not so good when the concentration of one of the reactants is several orders of magnitude larger than the other

Question: So what happens if the product can essentially 'decompose' back down to its base constituents?

Reversible Reactions



→ we assume the molecules of C can break apart at a rate (k_-) that is proportional to the concentration of C [in the spirit of the LMA!]

⇒ what we'll end up with now is a system of coupled (nonlinear) first order ODEs!!

4/6/10 (cont.)

- notice in the irreversible case, we only wrote an expression for c , but could have also written one for a and b :

$$\frac{da}{dt} = -k_{ab} = \frac{db}{dt} \quad (\text{think of this as an outflow due to the minus sign})$$

→ that is, anytime a (or conversely b) is 'lost' to make c , the change must ultimately be balanced (i.e. inflow - outflow = rate of change)

- in the reversible case, the 'inflow' for a and b is no longer zero since c can 'break apart' into the constituent A and B . Thus, logically we have the following system (built upon the idea stemming from the LMA):

$$\frac{dc}{dt} = k_{+}ab - k_{-}c$$

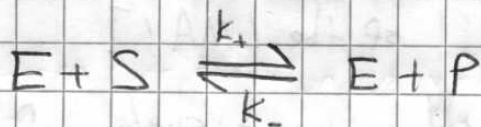
$$\frac{da}{dt} = k_{-}c - k_{+}ab$$

$$\frac{db}{dt} = k_{-}c - k_{+}ab$$

→ note that we still have $\frac{da}{dt} = \frac{db}{dt} = -\frac{dc}{dt}$ as we had in the irreversible case, but now each equation has an additional term and is directly coupled to all the other variables (and subsequently, there is an additional equilibrium solution)

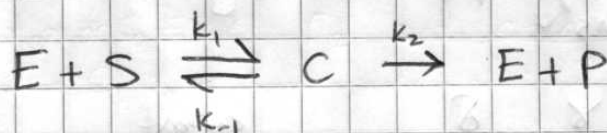
Michaelis-Menten Kinetics

- in other types of reactions, what is called an enzyme (E) reacts w/ a substrate (S) to create a product (P) plus a released enzyme



one modification to this is to have an intermediate step such that there is a 'catalyzer' (C):

NOTE: sometime C is indicated as ES



[this is called the Michaelis-Menten kinetic]

where k_1 , k , and k_2 are constants. Rewriting as a system of ODEs, we have:

$$\frac{ds}{dt} = -k_1 se + k_{-1} c$$

$$\frac{de}{dt} = -k_1 se + k_{-1} c + k_2 c$$

$$\frac{dc}{dt} = k_1 se - k_{-1} c - k_2 c = -\frac{de}{dt}$$

$$\frac{dp}{dt} = k_2 c$$

→ determining a solution to this system (so to derive the 'Michaelis-Menten equation') will form the basis of our final lab in 250B

Population Dynamics

another useful and popular place where a system of two (autonomous) first order ODEs manifests is in describing the rate of change of two interacting species. Consider:

$$\dot{x} = \alpha x + \beta xy$$

$$\dot{y} = \gamma y + \delta xy$$



4/6/10 (cont.)

where $x(t)$ and $y(t)$ might represent the population densities of species S_x and S_y respectively. α, β, γ and δ are constants and depending upon their sign, we can get different types of 'interactions'

α	β	γ	δ	context
+	+	+	-	predator (x) - prey (y) model
+	+	-	-	
-	+	+	-	
-	+	-	-	
				mutualism or symbiosis models
+	+	+	+	
+	+	-	+	
-	+	-	+	competition models
+	-	+	-	
+	-	-	-	
-	-	-	-	

for example, consider the following system:

$$\dot{x} = \overbrace{-ax}^{\text{too many predators! means no food!}} + \underbrace{bxy}_{\text{encounters w/ prey means something to eat!}}$$

$$\dot{y} = \underbrace{cy}_{\text{prey reproduce (that's what they do!)}} - \underbrace{dxy}_{\text{interactions w/ predators means prey get eaten!}}$$

x - predator (e.g. fox)
 y - prey (e.g. rabbit)
 $a, b, c, d > 0$

→ each term carries a unique meaning as listed above
 (these eqns. are known as the LOTKA VOLTEERRA EQNS.)