Simulating Chemical Reactions

- If lots of molecules ODE is accurate model - gives rate equations

We assume particles of X and Y are randomly spread in volume V. Their concentrations are $[X]$ and $[Y]$.

- The probability a particular particle Y_i is in small volume δV is $P(Y_i \in \delta V) = \frac{\delta V}{V}$

The probability of this reaction occurring relates to the number of molecules in a certain volume. i.e. close enough to react

- With n particles of type Y the probability of there being at least one in a small volume δV is
- $\frac{n\delta V}{V} = [Y]\delta V$
- with m particles of type X the probability of there being X_1 and X_2 in a small volume δV is:
- $\frac{m(m-1)}{2}\left(\frac{\delta V}{V}\right)^2 \approx \left(\frac{\delta V}{V}\right)^2 [X]^2$
- So the probability of there being one Y and two X in δV is $\propto [Y][X]^2(\delta V)^3$
- The number of δVs in total volume V is $N = \frac{\delta V}{V}$
- So the probability of the reaction in V is $\propto N[Y][X]^2(\delta V)^3 = V[[Y][X]^2(\delta V)^2$

$$2X + Y \xrightarrow{k_1} Z \tag{1}$$

i.e. the expected number of reactions per unit volume is $\propto [Y][X]^2$
The rate of formation of Z is:

$$\frac{d[Z]}{dt} = k_1[Y][X]^2 \tag{2}$$

The rate of formation of Y is:

$$\frac{d[Y]}{dt} = -k_1[Y][X]^2 \tag{3}$$

The rate of formation of X is:

$$\frac{d[X]}{dt} = -k_1[Y][X]^2 \tag{4}$$

So for these equations, what are the rate equations?

Equation	Rate of formation of X	Rate of formation of Y
$\emptyset \xrightarrow{k_1} X$	$\frac{d[X]}{dt} = k_1$	
$X \xrightarrow{k_2} Y$	$\frac{d[X]}{dt} = -k_2[X]$	$\frac{d[Y]}{dt} = k_2[X]$
$2Y \xrightarrow{k_3} X$	$\frac{d[X]}{dt} = k_3[Y]^2$	$\frac{d[Y]}{dt} = k_3[Y]^2$
$X \xrightarrow{k_4} 2Y$	$\frac{d[X]}{dt} = -k_4[X]$	$\frac{d[Y]}{dt} = 2k_4[X]$
$2X + Y \xrightarrow{k_5} 3X$	$\frac{d[X]}{dt} = 3k_5[X]^2[Y] - 2k_5[X]^2[Y]$ $\therefore \frac{d[X]}{dt} = k_5[X]^2[Y]$	$\frac{d[Y]}{dt} = -k_5[X]^2[Y]$

To combine a system of equations, you just add up the contributions to the rate of formation:

$\emptyset \xrightarrow{k_1} X$	$\frac{d[X]}{dt} = k_1$		
$\emptyset \xrightarrow{k_2} Y$		$\frac{d[Y]}{dt} = k_2$	
$X + Y \xrightarrow{k_3} Z$	$\frac{d[X]}{dt} = -k_3[X][Y]$	$\frac{d[Y]}{dt} = -k_3[X][Y]$	$\frac{d[Z]}{dt} = k_3[X][Y]$
$Z \xrightarrow{k_4} X + Y$	$\frac{d[X]}{dt} = k_4[Z]$	$\frac{d[Y]}{dt} = k_4[Z]$	$\frac{d[Z]}{dt} = -k_4[Z]$

Resulting in :

$$\frac{d[X]}{dt} = k_1 - k_3[X][Y] + k_4[Z] \tag{5}$$

$$\frac{d[Y]}{dt} = k_2 - k_3[X][Y] + k_4[Z] \tag{6}$$

$$\frac{d[Z]}{dt} = k_3[X][Y] - k_4[Z] \tag{7}$$