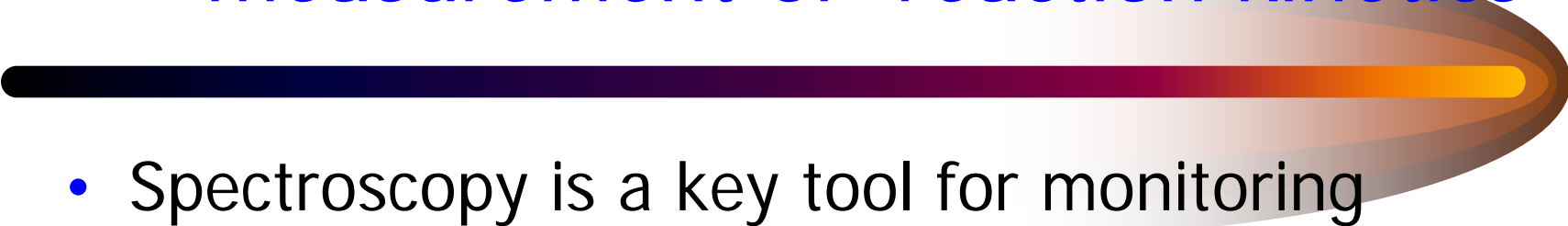# *Experimental Techniques*

- Monitor reaction progress using pressure, conductivity, spectrophotometry, etc. in real time.

- Quench reaction after a given time by rapid cooling or solvent trapping.

- Initiate process by flow, stopped-flow, rapid mixing or flash photolysis.

Time scales for experimental measurement of reaction kinetics

- Spectroscopy is a key tool for monitoring reaction progress on rapid time scales.

- Flash photolysis is a convenient method for initiating a time-dependent process with real-time acquisition as rapid as ten femtoseconds.

- Rapid mixing flowed reactions can be monitored at fixed distances with 100 μs time resolution.

- Stopped-flow has a 1 ms mixing time.

- Quenching method suitable for slow reactions.

Definition of rate

- For any given reaction, e. g. $A + B \rightarrow C$
- Rate of consumption of A is $v = -d[A]/dt$ where v stands for velocity.
- Rate of formation of C is $v = d[C]/dt$.
- Sign convention, reactants are consumed and therefore $d[\text{Reactant}]/dt < 0$.
- In general for any species $v = 1/n_j d[J]/dt$ where n_j is the stoichiometric coefficient.

Rates of appearance

- For a chemical reaction $d[J]/dt = n_j v$ where n_j is the stoichiometric coefficient.

- Example: $A + 2B + 3C \rightarrow D + 2E$

- If $d[A]/dt = v$, then the rate of disappearance is $d[B]/dt = 2v$, $d[C]/dt = 3v$ and the rate of appearance is $d[D]/dt = v$ and $d[E]/dt = 2v$.

Rates of appearance

- For a chemical reaction $d[J]/dt = n_j v$ where n_j is the stoichiometric coefficient.

- Example: $A + 2B + 3C \rightarrow D + 2E$

- If $v = -d[A]/dt$, $2v = -d[B]/dt$, $3v = -d[C]/dt$ then $v = d[D]/dt$ and $2v = d[E]/dt$ using the correct sign convention.

Rate Law

The rate is proportional to concentrations. Example: The rate law is v = k[A][B] where each reactant is raised to the first power. The coefficient k is called the rate constant.

The rate law can be determined by the isolation method. The reaction is run in an excess of all but one reactant to determine the dependence on concentration.

Units of the rate constant

The units of rate constant are always such that they convert into a rate expressed as concentration divided by time.

Rate $\quad=\quad$ k $\quad\quad$ [A] $\quad$ [B]

$(mol\ L^{-1}\ s^{-1}) = (L\ mol^{-1}\ s^{-1})(mol\ L^{-1})(mol\ L^{-1})$

Rate $\quad=\quad$ k $\quad\quad$ $[A]^2$ $\quad$ [B]

$(mol\ L^{-1}\ s^{-1}) = (L^2\ mol^{-2}\ s^{-1})(mol^2\ L^{-2})(mol\ L^{-1})$

Reaction Order

• The power to which a the concentration of a species is raised in the rate law is the reaction order. The overall order is the sum of all of the powers of all reactants.

Examples:

1. $v = k[NO]^2[O_2]$ First order in O_2, Second order in NO, Third order overall.

2. $v = k[A]^{1/2}[B]^2$ Half order in A, Second order in B, 2 1/2 order overall.

• The order does not need to be an integer.

Molecularity

Reaction order is an empirical quantity.
Molecularity refers to an elementary reaction
as a step in a reaction mechanism.
The rate law of an *elementary step*
can be deduced directly from the reaction.
Unimolecular reactions are first order.
A $\rightarrow$ Products   d[A]/dt = -k[A]
Bimolecular reactions are second order.
A + B $\rightarrow$ Products   d[A]/dt = -k[A][B]

An example: $2NO + O_2 \rightarrow 2NO_2$

The formation of nitric oxide is a termolecular reaction, i.e. three molecules must collide in order for the products to be formed. In this example the reaction is also the elementary step and so the rate law is $v = k[NO]^2[O_2]$ as stated earlier. In this case the reaction is third order *because of the fact that three molecules must combine simultaneously.* However, the reaction stoichiometry may not always indicate the molecularity of the reaction.