We can use *collision theory* to make predictions about the rates of the elementary processes. According to collision theory, a reaction results only if the reactants collide with sufficient energy and a favourable alignment. Not all collisions will lead to a reaction!

Key idea:	**Rate of an elementary process**	$\propto z \times f \times p$

z: collision frequency — collision frequency is proportional to the conc'n of each reactant molecule

f: fraction of collisions with enough KE to cause rx.

p: fraction of collisions with correct alignment

A. Rate Laws for elementary processes

Collision theory tells us that the rate law for an elementary process is determined by the number of reactant molecules involved in the process.

∴ Rate = const. [A][B (const. × f × p = "k")

Elementary Process	**Rate Law**	
A → products	Rate = $k[A]$	unimolecular process
A + A → products	Rate = $k[A]^2$	bimolecular processes
A + B → products	Rate = $k[A][B]$	bimolecular processes
A + A + A → products	Rate = $k[A]^3$	termolecular processes
2 A + B → products	Rate = $k[A]^2[B]$	termolecular processes
A + B + C → products	Rate = $k[A][B][C]$	termolecular processes

Question: Why can't we write down the rate law for all reactions using the rules above?

When we are given the overall rx. only (i.e. without knowing the mechanism), we don't know whether the rx. occurs directly (in a single elementary process) or as the result of two or more elementary processes.

B. From Mechanism to Rate Law

We shall now investigate how we combine the rate laws for individual elementary processes to deduce the rate law for the overall reaction. This is an important skill for a chemist to develop. (We must be able to derive the rate law for the mechanism to decide whether the proposed mechanism is consistent with the observed rate law.)

There are two cases to consider:

(1) We make assumptions about (or are told) which step in the mechanism is the slowest.

the appearance of products is limited by the slowest step in the sequence.

Strategy: Rate of the overall rx. ≈ rate of the slowest step

∴ The rate law for the overall rx. is determined by the rate law for the slowest step.

(2) We make no assumptions about which steps are fast or slow.

i.e. assuming all steps occur at comparable rates.

Strategy:

① Pick any reactant (or product) appearing in the overall rx.

② Identify steps in the mechanism that involve that particular reactant (or product)

③ Combine the rate laws for those steps algebraically to get the rate law for the overall rx.

We can save considerable effort if we pick a reactant or product that is involved in a small # of steps.