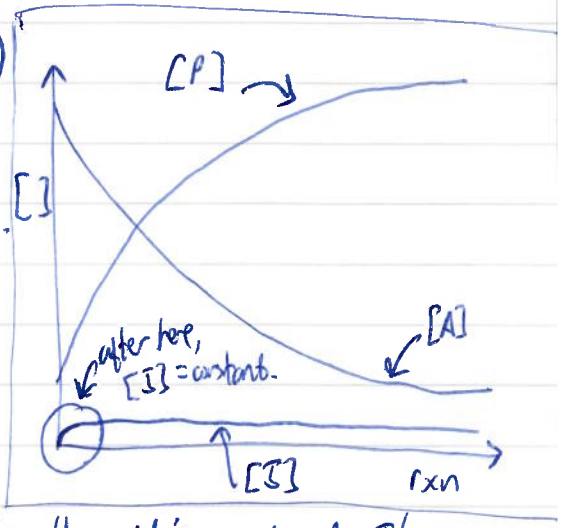
USEFUL APPROXIMATIONS IN KINETICS

The Steady-State Approximation (SSA)



Consider: $A \xrightarrow{k_1} I \xrightarrow{k_2} P$ (A: reactant, I: intermediate, P: product)

- This is a 2-step reaction.
- Multi-step reactions tend to have complex rate laws, so we need to simplify them.

If $k_1 << k_2$, then I is consumed much faster than it is produced. This means that [I] stays at a constant (low) level, after an initial "warm-up" period → see on graph above.

Mathematically, this means [I] doesn't change over time, i.e.

the SSA ↷ $\boxed{\frac{d[I]}{dt} = 0}$ only if $\boxed{k_1 << k_2}$ (i.e. k_1 = RDS)

Pre-Equilibria

Consider: $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \xrightarrow{k_2} P$ (A + B: reactants, I: intermediate, P: product) → reversible first step.

- If $k_2 << k_{-1}$, then I turns back into A+B faster than it turns into P
- The depletion of I into P (k_2) is slow, and any I lost to becoming P is quickly replaced by A+B → this means A+B and I are maintained in equilibrium.
- Recall, at equilibrium: $\boxed{\text{rate (forward rxn)} = \text{rate (backward rxn)}}$ ← IMPORTANT!

Therefore: rate (A+B → I) = rate (I → A+B)

and: $\boxed{k_1[A][B] = k_{-1}[I]}$ only if $\boxed{k_2 << k_{-1}}$

This helps us find [I] and simplify