Topic 5.9: Steady-State Approximation

Revision Notes · AP Chemistry

UNIT 5 · KINETICS

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An Intermediate in a Steady State

An intermediate is formed in one step of a mechanism and consumed in a later step (Topic 5.7). It is never poured into the vessel and never collected at the end.

After a very short opening period, an intermediate is consumed almost as fast as it is formed. Its concentration settles at a small value and stays nearly constant for most of the reaction.

That condition is called a steady state, written $d[I]/dt \approx 0$. The concentration is not zero, and it is not exactly constant: it is small enough, and steady enough, that its rate of change can be treated as zero.

The steady state matters because it ties the intermediate to the measurable reactants. If [I] is fixed by a balance between its formation and its consumption, that balance can be solved for [I], and the intermediate disappears from the rate law.

Topic 5.8 met the commonest case, a fast equilibrium before the slow step. These notes work that pre-equilibrium case in full, then the general case in which no equilibrium exists.

When the Pre-Equilibrium Approximation Applies

The pre-equilibrium approximation applies when a fast reversible step comes before the slow step.

The fast step reaches equilibrium almost at once. The slow step then drains the intermediate so slowly that the fast step's forward and reverse rates stay balanced: the equilibrium is maintained throughout the run.

The intermediate concentration is therefore set by the fast step's equilibrium constant and the reactant concentrations, not by the slow step at all.

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Signals in a question: a fast step written with ⇌ before a step labelled slow, a slow step whose rate law contains an intermediate, or an experimental rate law with an unexpected order or a species in the denominator.

The approximation does not apply if the slow step comes first: then its own law is already the finished law (Topic 5.8). It also fails if the early step is fast but one-way, because no equilibrium is established; that case needs the general steady-state treatment below.

The Substitution Method

First move: write the rate law of the slow step from its own reactants (Topic 5.4). It will contain the intermediate, so it cannot be the final answer.

Second move: write the equilibrium constant expression for the fast step, products over reactants, each concentration raised to the power of its coefficient in the step. Rearrange it to give the intermediate concentration in terms of reactants.

Third move: substitute that expression into the slow step's law. The constants k and K merge into a single overall constant, written k' = kK.

Check the result before trusting it: no intermediate anywhere, every species measurable, and only one constant. The same algebra works wherever a species forms in a fast equilibrium before reacting: an enzyme E binding its substrate S gives the complex ES, with [ES] = K[E][S] and rate = k'[E][S] for forming product.

Worked Examples

Example 1: The standard substitution. Step 1: $2NO \rightleftharpoons N_2O_2$ (fast, K). Step 2: $N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow, k_2). The slow step gives rate = $k_2[N_2O_2][H_2]$, with the intermediate N_2O_2 in it. From step 1, $K = [N_2O_2]/[NO]^2$, so $[N_2O_2] = K[NO]^2$. Substituting: rate = $k'[NO]^2[H_2]$, second order in NO, first order in H_2, third order overall. With K = 4.0 L/mol and k_2 = 25 L mol^{-1} s^{-1}, $[N_2O_2] = 4.0 \times (0.040)^2 = 6.4 \times 10^{-3}$ mol/L at [NO] = 0.040 mol/L, and with $[H_2]$ = 0.020 mol/L both the step law and the finished law give rate = 3.2×10^{-3} mol L^{-1} s^{-1}.

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Example 2: A species in the denominator. Step 1: A + B ⇌ C + D (fast, K = 0.50). Step 2: C → E (slow, k = 0.10 s^{-1}). Here the equilibrium makes a co-product D alongside the intermediate C, so K = [C][D]/[A][B] gives [C] = K[A][B]/[D]. Substituting into rate = k[C] gives rate = k'[A][B]/[D]: first order in A and in B, and negative first order in D. With [A] = 0.20, [B] = 0.10 and [D] = 0.40 mol/L, [C] = 0.025 mol/L and both laws give rate = 2.5 × 10^{-3} mol L^{-1} s^{-1}. The negative order is real: adding D pushes the fast equilibrium backwards, lowers [C], and slows the reaction. An experimental law with a denominator species is the fingerprint of a fast equilibrium that produces that species.

Example 3: The effective constant k' = kK. Step 1: A + B ⇌ C (fast, K = 2.5 L/mol). Step 2: C + D → E (slow, k_2 = 0.40 L mol^{-1} s^{-1}). The finished law is rate = k'[A][B][D] with k' = k_2K = 0.40 × 2.5 = 1.0 L^2 mol^{-2} s^{-1}: the units multiply just as the values do, and they must match the overall order, here third. At [A] = 0.10, [B] = 0.20 and [D] = 0.10 mol/L, [C] = 2.5 × 0.10 × 0.20 = 0.050 mol/L, and the step law and the finished law both give rate = 2.0 × 10^{-3} mol L^{-1} s^{-1}.

Example 4: The general steady state, with no equilibrium. Step 1: A + B → I (fast but one-way, k_1 = 0.40 L mol^{-1} s^{-1}). Step 2: I + C → P (slow, k_2 = 2.0 × 10^2 L mol^{-1} s^{-1}). No equilibrium constant exists, so use the steady state directly: the rate of forming I equals the rate of consuming it, k_1[A][B] = k_2[I][C], which gives [I] = k_1[A][B]/(k_2[C]). Substituting into rate = k_2[I][C], the k_2 and the [C] cancel, leaving rate = k_1[A][B]. At [A] = 0.10, [B] = 0.050 and [C] = 0.020 mol/L, [I] = 5.0 × 10^{-4} mol/L, reassuringly small next to the reactant concentrations, and the rate is 2.0 × 10^{-3} mol L^{-1} s^{-1} by both routes.

Traps That Cost Marks in Topic 5.9

Handing in the slow step's law. A law containing an intermediate is the starting point of the method, not its answer. The substitution is the question.

Forgetting the co-product. When the fast step produces C + D together, solving for [C] brings [D] into the denominator. Dropping it loses the negative order and the mark.

Writing K upside down. K is products over reactants, powers equal to coefficients: for 2NO ⇌ N_2O_2, K = $[N_2O_2]/[NO]^2$. Inverting it inverts every order that follows.

Leaving two constants in the finished law. k and K never both survive. They merge into one constant, k' = kK, whose units are the product of the two sets of units.

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Using pre-equilibrium where it does not belong. A slow first step needs no substitution at all, and a fast one-way step provides no K. Check the arrows and the labels before choosing the method.

Rejecting a negative order as a mistake. A species in the denominator is a genuine result: it is a product of the fast equilibrium, and raising its concentration really does slow the reaction.

Key Relationships to Remember

- Steady state: d[I]/dt ≈ 0, because the intermediate is consumed about as fast as it is formed, so its concentration stays small and nearly constant
- Pre-equilibrium: a fast reversible step before the slow step holds the intermediate at its equilibrium concentration while the slow step runs
- Substitution: solve the fast step's K expression for [I], substitute into the slow step's law, and fold the constants into one, k' = kK
- A finished rate law contains no intermediate and only one constant; its units must match its overall order
- A co-product of the fast equilibrium lands in the denominator of the finished law, giving a negative order in that species
- No equilibrium before the slow step: set the intermediate's formation rate equal to its consumption rate and solve for [I] instead
- The finished law's orders come from the substitution, so they can be higher than the slow step's own orders

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Topic 5.9 Worksheet

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