**Question:** State, with explanation, which diagram corresponds to $k_a \gg k_b$.

Assuming 1st order reactions for both of the two steps, it is possible to solve the rate equations analytically,[*] which gives

$$
\begin{cases}
[A]_t = [A]_0 e^{-k_a t} \\[2mm]
[B]_t = \dfrac{k_a}{k_a - k_b}(-e^{-k_a t} + e^{-k_b t})[A]_0 \\[2mm]
[C]_t = \left(1 + \dfrac{1}{k_a - k_b}(k_b e^{-k_a t} - k_a e^{-k_b t})\right)[A]_0
\end{cases}
$$

The mathematical derivation is far beyond the assumed level of this course. The reason for showing these equations is because the formula for $[C]_t$ is useful to demonstrate the

---

[*] The rate equations for this scheme are:

$$
\frac{dA}{dt} = -k_a A, \qquad \frac{dB}{dt} = k_a A - k_b B, \qquad \frac{dC}{dt} = k_b B
$$

The first equation for $A(t)$ is the same as what we have seen previously in Sec 3.1.2. We put the solution $A(t) = A(0)e^{-k_a t}$ in the second equation. This yields an ordinary differential equation for $B(t)$, for which the solution method is well established (though we have no space to expand it here). $C(t)$ can be obtained from a relation $A(t) + B(t) + C(t) = \text{constant} = A(0)$, which describes the conservation of gross materials.

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concept of **rate-determining step**, as will be discussed next.

## 4.4  Rate-determining process

The above formula for $[C]_t$ can be simplified in two limiting cases where one of the rate constants is much larger than the other. For example, when $k_a \gg k_b$, we find $e^{-k_a t} \ll e^{-k_b t}$ and $1/(k_a - k_b) \simeq 1/k_a$. Therefore, $[C]_t$ can be simplified as

$$[C]_t \simeq (1 - e^{-k_b t})[A]_0$$

This means that the behaviour of $[C]_t$ is determined by the rate constant of the slower step $k_b$.

**Question:**  Show that when $k_a \ll k_b$,

$$[C]_t \simeq (1 - e^{-k_a t})[A]_0$$

In this way, the slower step determines the overall rate of the product formation. This is called the **Rate-determining** or **Rate-limiting** step. The idea is straightforwardly generalized for reactions involving more than two steps, i.e., more than one intermediates $I_1, I_2, \cdots$, involved between the reactant R and product P:

$$R \rightarrow I_1 \rightarrow I_2 \rightarrow \cdots \rightarrow P$$
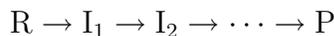
## 5  Steady-state approximation

It is seen in the right panel of the previous diagram that the concentration of B does not change much but stays low and nearly constant, and therefore $d[B]/dt \simeq 0$, when $k_b \gg k_a$, i.e., when this intermediate specie is highly reactive. This suggests a very useful and powerful method called the **steady-state approximation**.

**Recipe of the Steady-State Approximation**

1. Identify reactive intermediates, $I_1, I_2, \cdots$, in the mechanism

2. Write down $\dfrac{d[I_i]}{dt}$ from the assumed mechanism.

3. Set $\dfrac{d[I_i]}{dt} = 0$ and solve for $[I_i]$. (The solution will be denoted by $[I_i]_{ss}$.)

4. Deduce, and simplify if possible, the rate law by using $[I_i]_{ss}$.

## 5.1 Application

Let us see how the steady-state approximation works for the following scheme

$$A \overset{k_f, k_b}{\rightleftharpoons} B \overset{k_r}{\to} P \tag{49}$$

which has been examined previously by invoking the pre-equilibrium approximation. The critical assumption there was the reaction from B to P is very slow such that it does not disturb very much the equilibrium between A and B. We will now relax this assumption. To this end, let us follow the recipe of the steady-state approximation. As before, we will assume that all the steps $k_f$, $k_b$ and $k_r$ are 1st order.

1. We identify B as the reactive intermediate.

2. Noting that B is gained by $k_f$ and lost by $k_b$ and $k_r$ steps,

$$\frac{d[\mathrm{B}]}{dt} = k_f[\mathrm{A}] - k_b[\mathrm{B}] - k_r[\mathrm{B}]$$

3. Set the above to be equal to zero, and solve for [B].

$$k_f[\mathrm{A}] - k_b[\mathrm{B}] - k_r[\mathrm{B}] \simeq 0 \quad \Rightarrow \quad [\mathrm{B}]_{\mathrm{ss}} = \frac{k_f}{k_b + k_r}[\mathrm{A}]$$

4. The overall reaction rate is that of the product formation described by the $k_r$ step. We write down this equation and then replace [B] by $[\mathrm{B}]_{\mathrm{ss}}$.

$$\mathrm{Rate} = \frac{d[\mathrm{P}]}{dt} = k_r[\mathrm{B}] \simeq k_r[\mathrm{B}]_{ss} = \frac{k_r k_f}{k_b + k_r}[\mathrm{A}] \tag{50}$$

Compare this with the result from the pre-equilibrium assumption, Eq (45):

$$\mathrm{Rate\ (pre\text{-}Eq)} \simeq k_r K[\mathrm{A}] = \frac{k_r k_f}{k_b}[\mathrm{A}]$$

The difference is in the denominator of the rate factor. Remember that the fundamental assumption in the pre-equilibrium case was $k_r \ll k_b$. This means that the denominator in Eq (50) may be approximated as $k_b + k_r \simeq k_b$. We therefore find that the pre-equilibrium approximation Eq (45) is reproduced as a limiting case of the steady-state approximation Eq (50). In other words, the steady-state approximation generalizes, and therefore covers broader applicability than, the pre-equilibrium approximation.