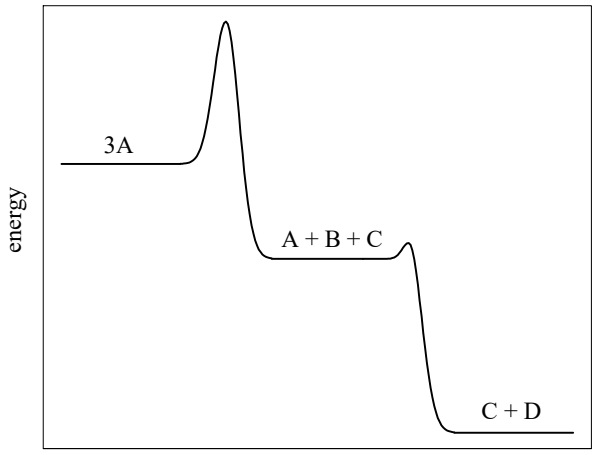
ChemE 2200 - Physical Chemistry II for Engineers

Quiz 10 - April 9, 2025

Name: *Solution*

(A) A key concept is that the first level and the last level must represent the overall reaction. Although only two As are consumed in the first reaction, a third A is needed for the second reaction. And the by-product C created in the first reaction must be carried to the last level.



(B) Start with an expression for the differential rate equation from the second elementary reaction.

$$\frac{d[\mathrm{D}]}{dt} = k_2[\mathrm{A}][\mathrm{B}]$$

Because B is an intermediate, [B] is not allowed in the rate equation. We need an expression for [B]. Because $k_1 + k_{-1} \ll k_2$, we assume the Steady-State Approximation for B, which yields the equation

$$\frac{d[\mathrm{B}]}{dt} = 0 = k_1[\mathrm{A}]^2 - k_{-1}[\mathrm{B}][\mathrm{C}] - k_2[\mathrm{A}][\mathrm{B}]$$

$$[\mathrm{B}] = \frac{k_1[\mathrm{A}]^2}{k_{-1}[\mathrm{C}] + k_2[\mathrm{A}]}$$

Substitute the expression for [B] into the rate equation.

$$\frac{d[\mathrm{D}]}{dt} = \frac{k_1 k_2[\mathrm{A}]^3}{k_{-1}[\mathrm{C}] + k_2[\mathrm{A}]}$$

It is incorrect to include a factor of 2 in the steady-state approximation. That is, it is incorrect to write

$$0 = 2k_1[\mathrm{A}]^2 - k_{-1}[\mathrm{B}][\mathrm{C}] - k_2[\mathrm{A}][\mathrm{B}]$$

Recall from the definition of reaction rate, the relation for the first reaction is

$$r_{\mathrm{rxn}} = \frac{1}{-2}\frac{d[\mathrm{A}]}{dt} = \frac{1}{1}\frac{d[\mathrm{B}]}{dt} = \frac{1}{1}\frac{d[\mathrm{C}]}{dt}$$

Because the forward and reverse reactions are elementary,

$$r_{\mathrm{rxn}} = k_1[\mathrm{A}]^2 - k_{-1}[\mathrm{B}][\mathrm{C}]$$

There is no factor of 2 in the expression for $d[\mathrm{B}]/dt$.

Grading Rubric:

+3: Each section of the reaction-coordinate energy-level diagram is correct

+2: Correct rate expression for [D]

+2: Correct assumption used to solve for intermediate → steady-state approximation

+2: Using the chosen assumption, solved for intermediate [B] and plugged back into the rate expression

+1: Correct final rate expression