

Question 9

In a closed, well-mixed vessel of constant volume, the reversible reaction $A \rightleftharpoons 2B$ has forward reaction rate $k_f a$ and reverse reaction rate $k_r b^2$ in $\text{mol}/(\text{L}\cdot\text{min})$, where a, b are concentrations in mol/L . Here $k_f = 1 \text{ min}^{-1}$ and $k_r = 1 \text{ L}/(\text{mol}\cdot\text{min})$. Initially $a = 1$, $b = 0 \text{ mol}/\text{L}$. There are no other reactions. Use numerical concentration values in these units.

Tasks

1. Derive the concentration equations from the stoichiometric coefficients. Identify a conserved weighted concentration and explain why $a + b$ is not conserved.
2. Reduce to a scalar equation for b and identify its physically allowed interval. Show this interval is invariant.
3. Find the unique physical equilibrium and prove the stated initial response approaches it monotonically in b .
4. Solve explicitly for $b(t)$ by separation, then recover $a(t)$. Explain why the second algebraic root of the equilibrium equation is inadmissible and why the physical equilibrium is not reached at finite time.

Question 9 – Solution

Strategy. Each forward reaction consumes one A and creates two B; the resulting weighted conservation law reduces the nonlinear system.

Step 1: Respect the reaction stoichiometry. A net forward reaction rate $a - b^2$ gives

$$\boxed{a' = -a + b^2, \quad b' = 2a - 2b^2}$$

in the chosen numerical units. Hence $(2a + b)' = 0$ and $\boxed{2a + b = 2}$ mol/L. The sum $a + b$ has derivative $a - b^2$ and is not conserved: the reaction changes the number of molecules, while preserving the weighted building-block total.

Step 2: Reduce within the physical domain. With $a = 1 - b/2$, the scalar equation is $\boxed{b' = 2 - b - 2b^2}$, with $0 \leq b \leq 2$ required by $a, b \geq 0$. At $b = 0$ the derivative is $2 > 0$, and at $b = 2$ it is $-8 < 0$. Uniqueness and inward boundary directions make the interval invariant. The concentrations cannot be extended to negative values merely because an algebraic equation has another root.

Step 3: Identify the attracting physical equilibrium. Let $d = \sqrt{17}$ and $r_{\pm} = (-1 \pm d)/4$. Then $b' = -2(b - r_+)(b - r_-)$, with $r_- < 0 < r_+ < 2$. The only physical equilibrium is

$$\boxed{b_* = r_+, \quad a_* = 1 - r_+/2.}$$

For $0 \leq b < r_+$, $b' > 0$. Uniqueness prevents crossing the equilibrium, so the solution from zero increases and stays below r_+ . Its limit must be a zero of the scalar right side; otherwise its positive derivative would remain bounded away from zero. Thus it tends to r_+ .

Step 4: Separate and impose the initial concentration. Since $2(r_+ - r_-) = d$, integration gives

$$\log \left| \frac{b - r_+}{b - r_-} \right| = -dt + \log \left| \frac{r_+}{r_-} \right|.$$

The ratio is negative on the physical branch starting at zero. Solving gives

$$\boxed{b(t) = \frac{r_+(1 - e^{-dt})}{1 - (r_+/r_-)e^{-dt}}, \quad a(t) = 1 - \frac{b(t)}{2}.}$$

The denominator exceeds 1 at finite times because $r_+/r_- < 0$. The formulas give $(a, b) = (1, 0)$ initially and the stated equilibrium as $t \rightarrow \infty$. For every finite t , $b < r_+$, so arrival is asymptotic.