A First Course on Kinetics and Reaction Engineering

Class 19 on Unit 18

Where We're Going

- Part I - Chemical Reactions
- Part II - Chemical Reaction Kinetics
- Part III - Chemical Reaction Engineering
  - A. Ideal Reactors
  - B. Perfectly Mixed Batch Reactors
    - 18. Reaction Engineering of Batch Reactors
    - 19. Analysis of Batch Reactors
    - 20. Optimization of Batch Reactor Processes
  - C. Continuous Flow Stirred Tank Reactors
  - D. Plug Flow Reactors
  - E. Matching Reactors to Reactions
- Part IV - Non-Ideal Reactions and Reactors

Reaction Engineering with Batch Reactors

- Operation
  - Clean
  - Prepare and Charge
  - Process according to Protocol
  - Drain
- Productivity
  - Turnaround time
  - Processing (reaction) time
- Reactor Design Problems
  - Sizing and Processing Protocol
  - Optimization
- Other Reaction Engineering Tasks
  - Simulate the entire process (e. g. for automating controls)
  - Evaluate the effect of some change in the protocol
- Reasons for using Batch Reactors
  - Flexibility
  - Small Quantities of Product
  - Precise Control
- Disadvantages
  - Labor Intensive
  - Batch to Batch Consistency
  - Not Suited to Producing Large Quantities
- Importance of Physical Understanding
  - You will retain your physical understanding much longer than an equations-based understanding
  - A physical understanding may allow you to eliminate some design alternatives without having to solve the design equations
  - It will be easier to make creative new (patentable) discoveries if you have a sound physical understanding

Major AFCoKaRE Problem Types and How to Identify Them

- Reaction Mechanism Problems
  - In a reaction mechanism problem one is typically given a macroscopically observed (also called overall or apparent) reaction along with a mechanism and asked to generate a rate expression for the macroscopically observed reaction rate.
- Age Function Problems
  - In an age function problem one is typically given data for the response of a laboratory reactor to either a step change or an impulse stimulus and asked to use those data to determine whether the laboratory reactor obeys the assumptions of one of the ideal flow reactor models (CSTR or PFR).
- Kinetics Data Analysis Problems
  - In a kinetics data analysis problem, one is typically given a set of kinetics data for a given reaction, the type of ideal reactor used to gather those data and a description of the reactor and how it was operated. One is then asked either to find a rate expression that describes the data, or, more commonly to test whether a given rate expression gives an accurate representation of the data.
- Qualitative Reaction Engineering Problems
  - In a qualitative reaction engineering problem, one is typically given the reaction(s) that is(are) taking place and some information about them along with the type of reactor being used and some information about how that reactor is operated. One is then usually asked to qualitatively describe or sketch how one (or more) quantities will vary during the operation of the reactor. In particular, one is not asked to calculate quantities or to plot calculated quantities (as opposed to making a qualitative sketch).

A General Approach to Solving Qualitative Reaction Engineering Problems

- Read through the problem statement and identify
  - the type(s) of reactor(s) being used
  - the reactor operating procedure being used (isothermal vs. adiabatic, steady state vs. transient, etc.)
  - the type of reaction(s) taking place (reversible/irreversible, typical, auto-catalytic, product inhibited, etc.)
  - the quantities whose variation you are asked to describe
- Sketch a plot of reactant concentration(s), product concentrations, temperature, reaction rate and other quantities of interest versus time (for a batch reactor) or space time (for a flow reactor)
  - Draw sets of axes for the plots
  - Determine the initial values of each of these quantities (at the start of the reaction or inlet to the reactor) and add to the corresponding plot

- Determine the initial slope of the plots of these quantities by considering the first small increment in time (or space time) and add to the corresponding plot
  - Do the reactant concentrations, product concentrations and temperature increase or decrease during this interval?
  - Will those changes cause the reaction rate to increase or decrease during this interval?
  - Do the quantities of interest increase or decrease during this interval?
  - Will those changes cause the equilibrium conversion to increase or decrease during this interval?
  - if comparing two or more systems, for each plot, determine the which system will have the largest slope, the second largest slope, etc.
- Determine the curvature of the plots by considering the next small increment in time (or space time) and add to the corresponding plot
  - Do the reactant concentrations, product concentrations, temperature and rate change by a greater or lesser amount than during the preceding interval?
  - Do the quantities of interest change by a greater or lesser amount than during the preceding interval?
- Determine whether continuing the initial trends will result in the rate asymptotically approaching equilibrium
  - If not, infer what must happen so that the system approaches equilibrium properly (i. e. so the rate progressively decreases to zero) and add to the corresponding plots
- If comparing two or more systems, determine the relative magnitudes of the equilibrium concentrations and temperatures in order to ascertain whether or not the curves for the systems being compared cross each other

- Use the plots to answer the questions posed in the problem

Questions?

Analysis of a Reactant-Inhibited Reaction

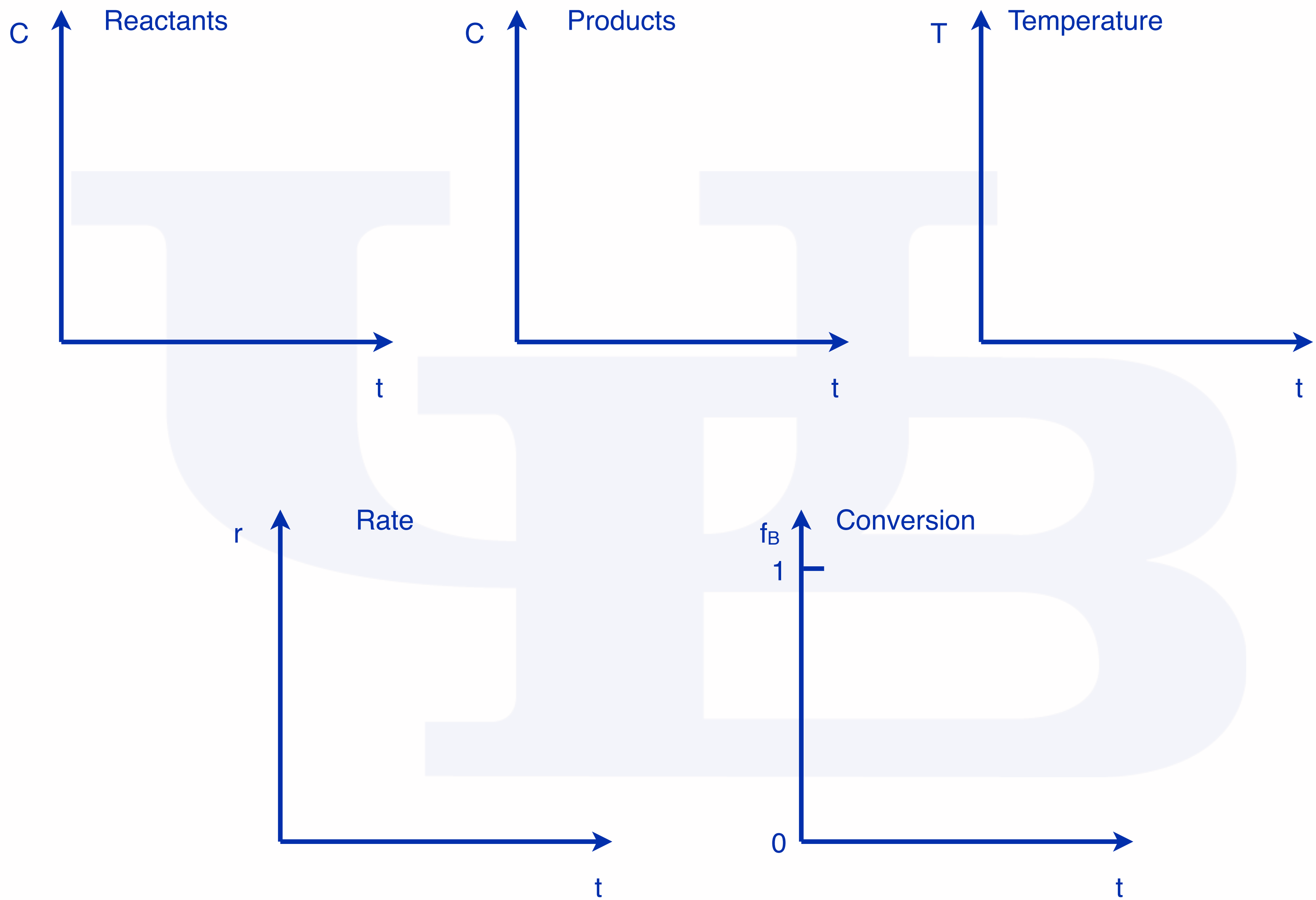
Suppose the catalytic reaction (1) below is reactant inhibited with a rate expression of the form shown in equation (2). The reaction is irreversible, and K is very, very small in magnitude. Predict, qualitatively, how the rate and the conversion will vary as a function of isothermal batch reaction time (a) if $P_A^0 = P_B^0$ and (b) if $P_A^0 > P_B^0$.

$$A + B \rightarrow Y + Z \qquad (1)$$

$$r = \frac{kP_B}{K + P_A} \qquad (2)$$

- In this problem we are given information about a reaction and the reactor in which that reaction takes place. We are asked to make qualitative predictions about the reactor's performance
    - This is a qualitative reaction engineering problem
- Read through the problem statement and identify
    - the type(s) of reactor(s) being used
    - the reactor operating procedure being used (isothermal vs. adiabatic, steady state vs. transient, etc.)
    - the type of reaction(s) taking place (reversible/irreversible, typical, auto-catalytic, product inhibited, etc.)
    - the quantities whose variation you are asked to describe

- Read through the problem statement and identify
  - the type(s) of reactor(s) being used: a batch reactor
  - the reactor operating procedure being used (isothermal vs. adiabatic, steady state vs. transient, etc.): isothermal, batch reactors are always transient
  - the type of reaction(s) taking place (reversible/irreversible, typical, auto-catalytic, product inhibited, etc.): irreversible reaction
  - the quantities whose variation you are asked to describe: want variations of r and f_A
- Sketch a plot of reactant concentration(s), product concentrations, temperature, reaction rate and other quantities of interest versus time (for a batch reactor) or space time (for a flow reactor)
  - Draw sets of axes for the plots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- Determine the initial values of each of these quantities (at the start of the reaction or inlet to the reactor) and add to the corresponding plot

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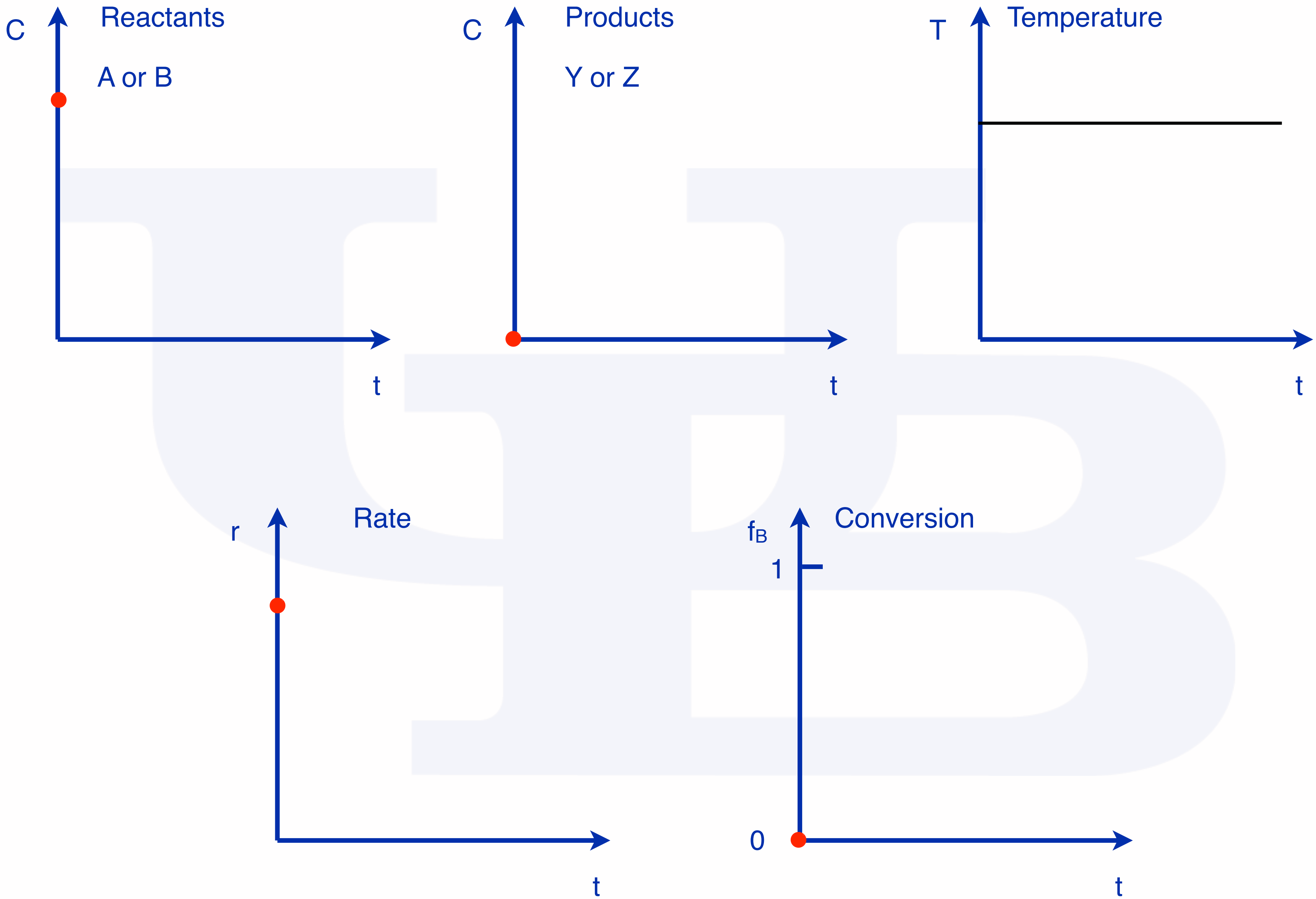
  - since the reactor is isothermal, we don't need to consider temperature
  - in case (a), both reactant concentrations are positive and equal, both reactant concentrations are zero, the rate is positive and the conversion is zero.
  - in case (b), both reactant concentrations are positive with A greater than B, both reactant concentrations are zero, the rate is positive and the conversion is zero.

Case (a)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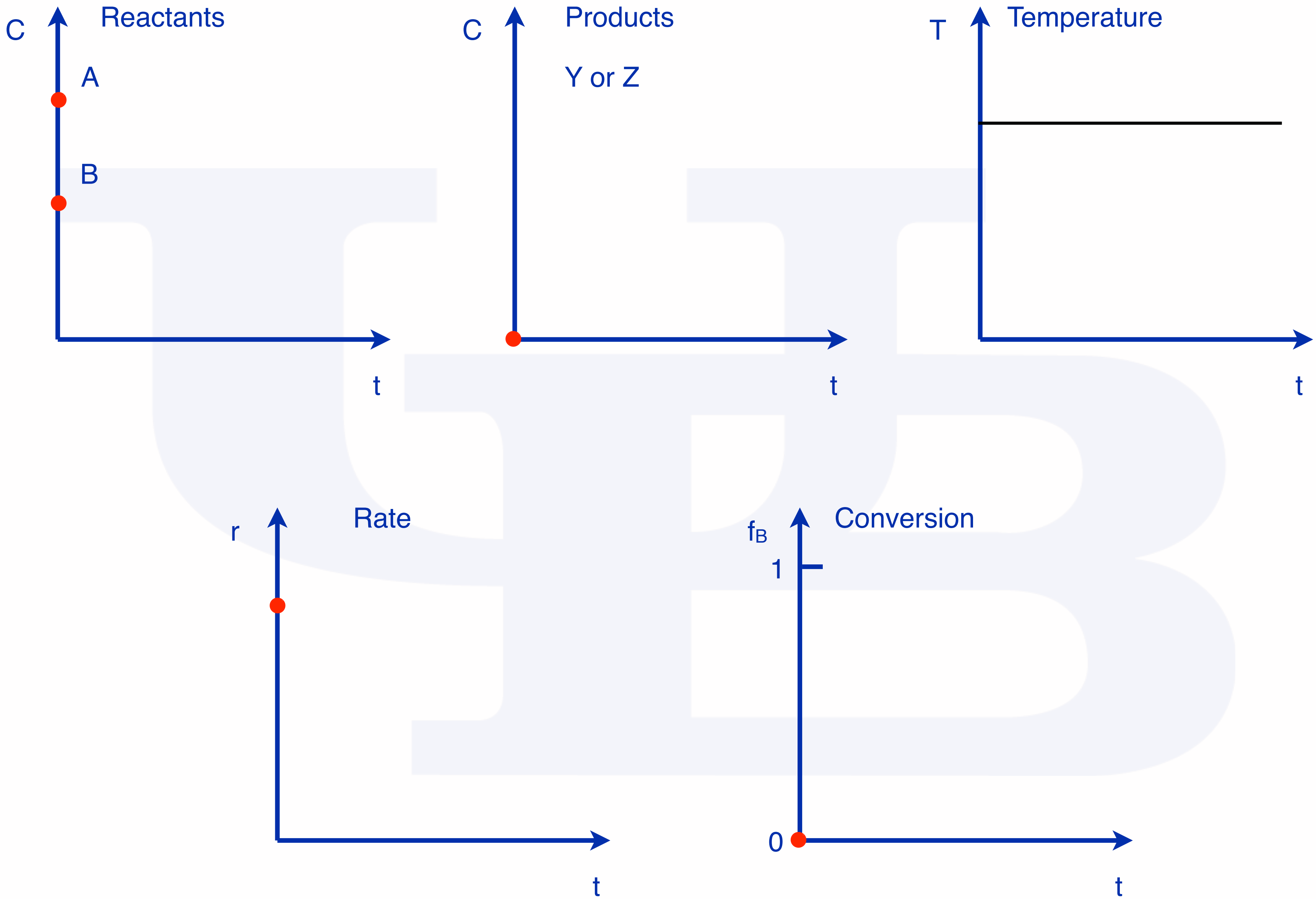
Case (b)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- Determine the initial slope of the plots of these quantities by considering the first small increment in time (or space time) and add to the corresponding plot
  - Do the reactant concentrations, product concentrations and temperature increase or decrease during this interval?
  - Will those changes cause the reaction rate to increase or decrease during this interval?
  - Do the quantities of interest increase or decrease during this interval?
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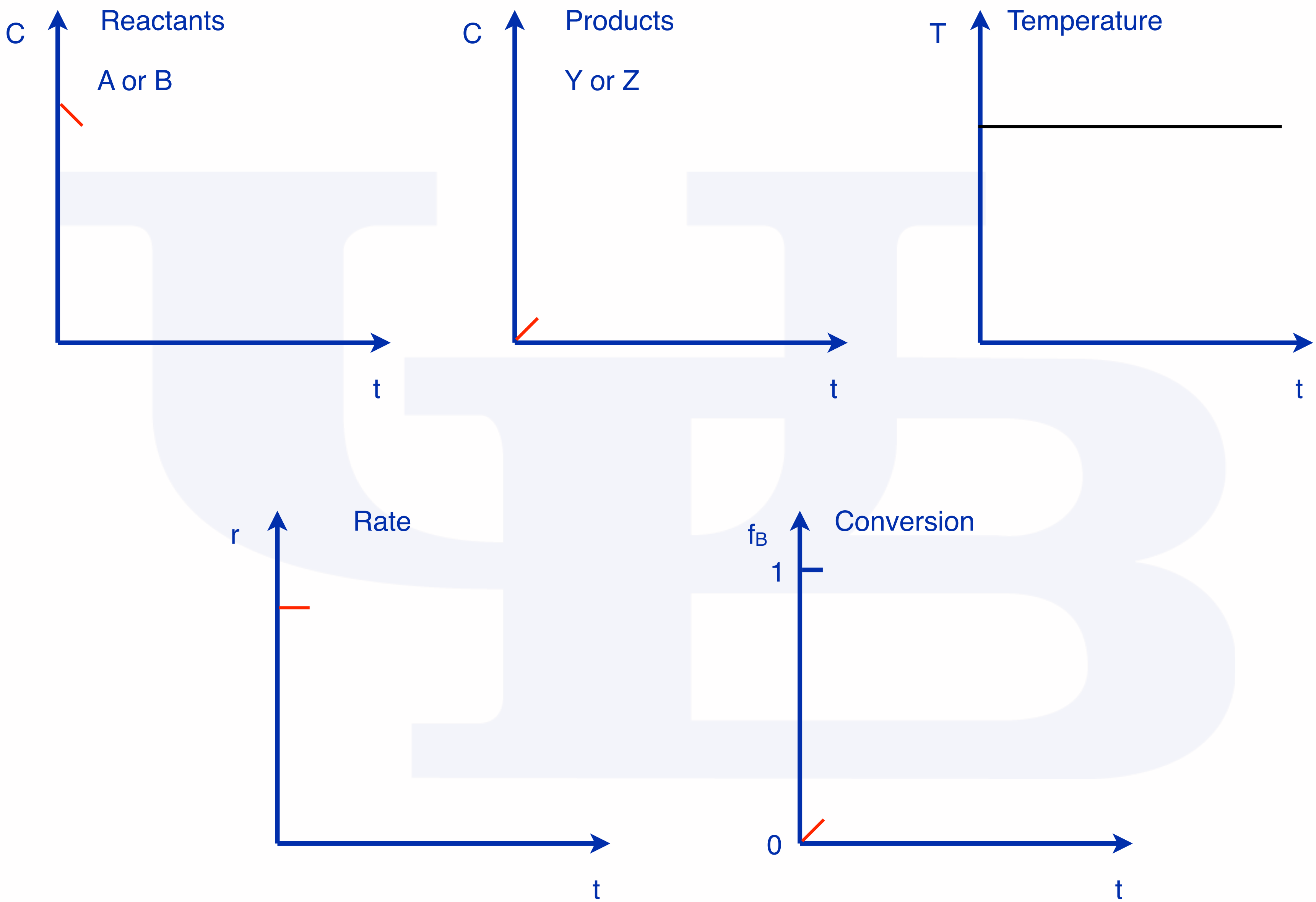
  - if comparing two or more systems, for each plot, determine the which system will have the largest slope, the second largest slope, etc.

- Determine the initial slope of the plots of these quantities by considering the first small increment in time (or space time) and add to the corresponding plot
  - Do the reactant concentrations, product concentrations and temperature increase or decrease during this interval?
    - in both cases the reactant concentrations decrease and the product concentrations increase
  - Will those changes cause the reaction rate to increase or decrease during this interval?
    - only the reactant concentration affect the rate
    - In case (a) the rate will stay the same because K is negligibly small and P_A and P_B will cancel
    - In case (b) the rate will decrease because the denominator will be ~ constant while the numerator decreases
  - Do the quantities of interest increase or decrease during this interval?
    - in both cases conversion will increase (initial slope positive)
  - Will those changes cause the equilibrium conversion to increase or decrease during this interval?
    - since the temperature is constant, the equilibrium conversion will not change during the reaction
  - if comparing two or more systems, for each plot, determine the which system will have the largest slope, the second largest slope, etc.
    - in case (a) the rate will approximately equal k, in case (b) it will approximately equal kP_B/K
    - we can't tell which rate is larger, so we can't determine the relative slopes for the 2 cases

Case (a)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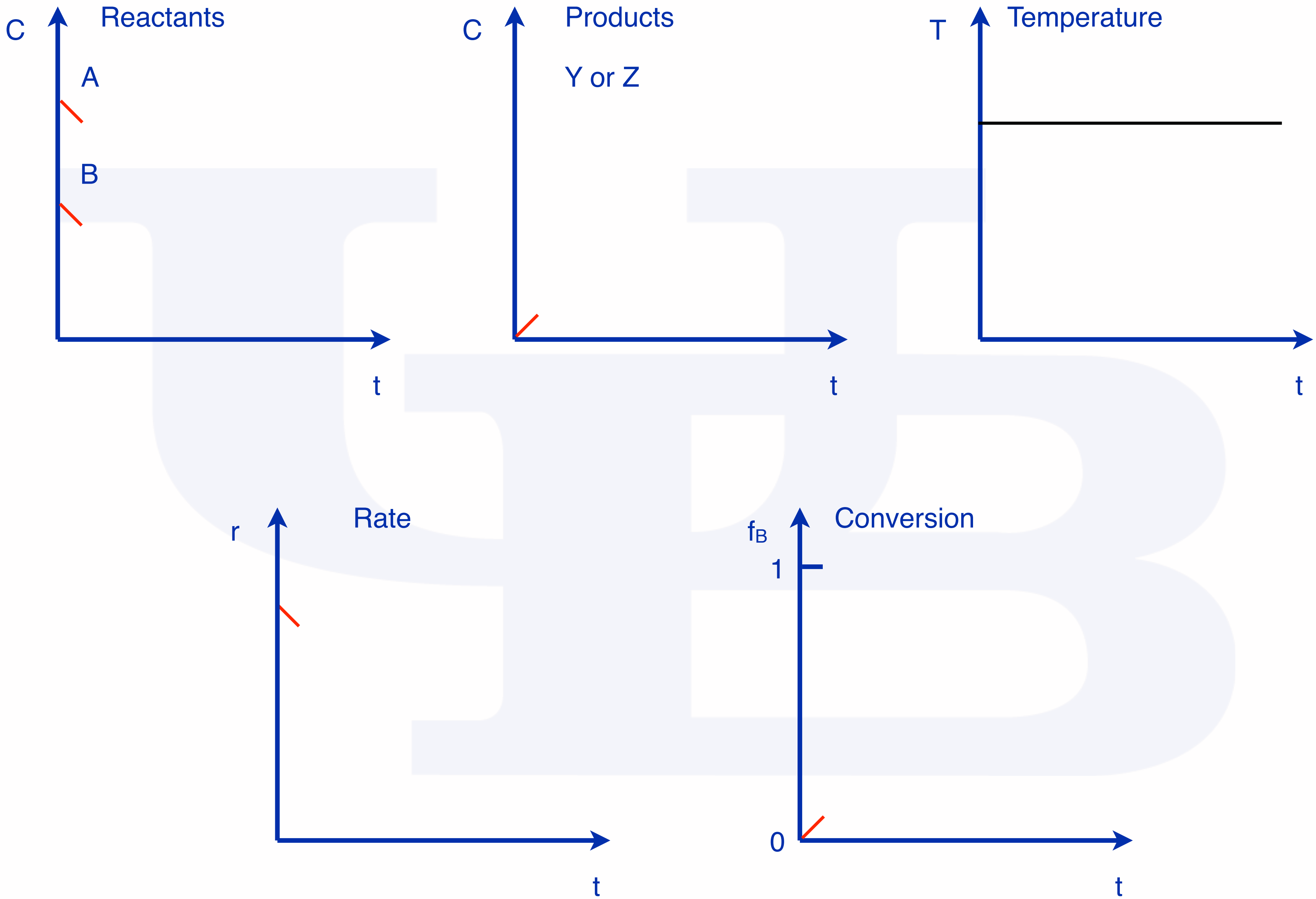
Case (b)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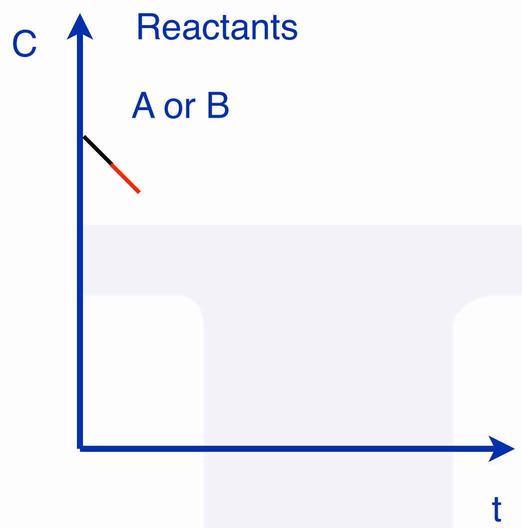
- Determine the curvature of the plots by considering the next small increment in time (or space time) and add to the corresponding plot
  - Do the reactant concentrations, product concentrations, temperature and rate change by a greater or lesser amount than during the preceding interval?
  - Do the quantities of interest change by a greater or lesser amount than during the preceding interval?

- Determine the curvature of the plots by considering the next small increment in time (or space time) and add to the corresponding plot
  - Do the reactant concentrations, product concentrations, temperature and rate change by a greater or lesser amount than during the preceding interval?
    - in case (a) the rate stays the same (no curvature)
      - the reactant concentrations decrease by the same amount (no curvature)
      - the product concentrations increase by the same amount (no curvature)
    - in case (b) the rate is smaller than in the previous interval
      - the reactant concentrations decrease by less (concave up)
      - the reactant concentrations increase by less (concave down)
      - since the reactant concentrations decrease by less, the rate will decrease by less (concave up)
  - Do the quantities of interest change by a greater or lesser amount than during the preceding interval?
    - in case (a) the conversion increases by the same amount (no curvature)
    - in case (b) the conversion will increase by less (concave down)

Case (a)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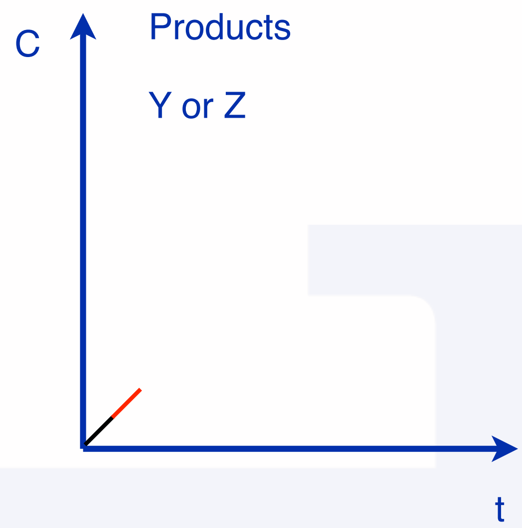
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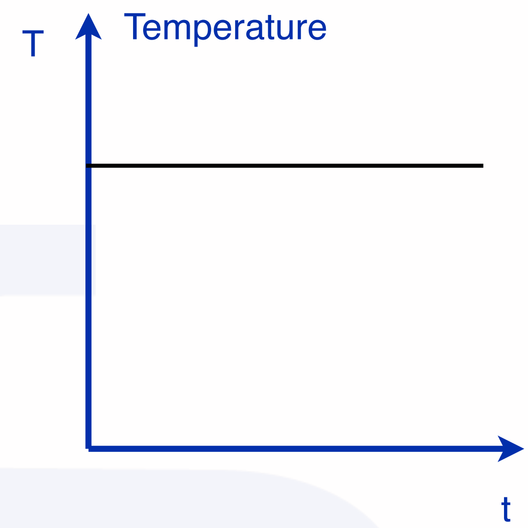
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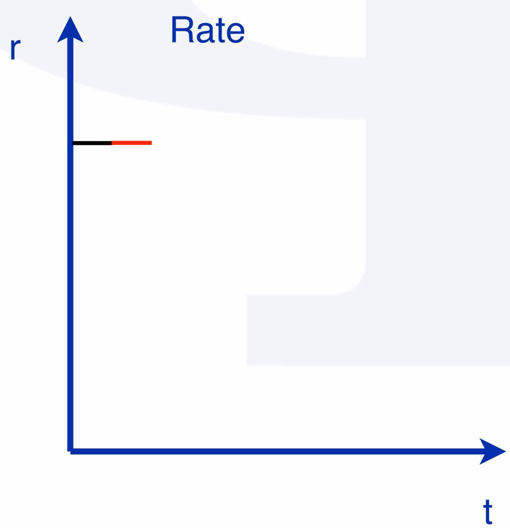
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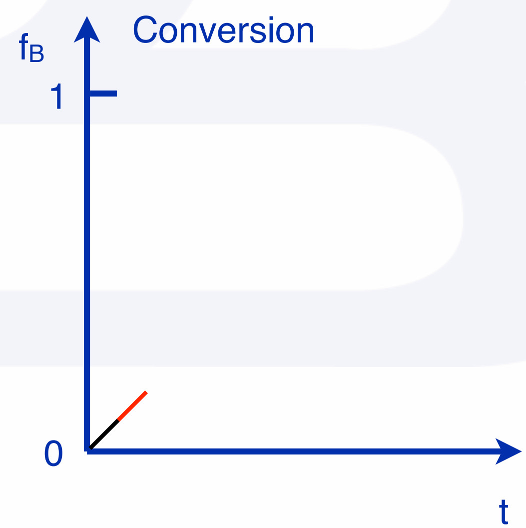
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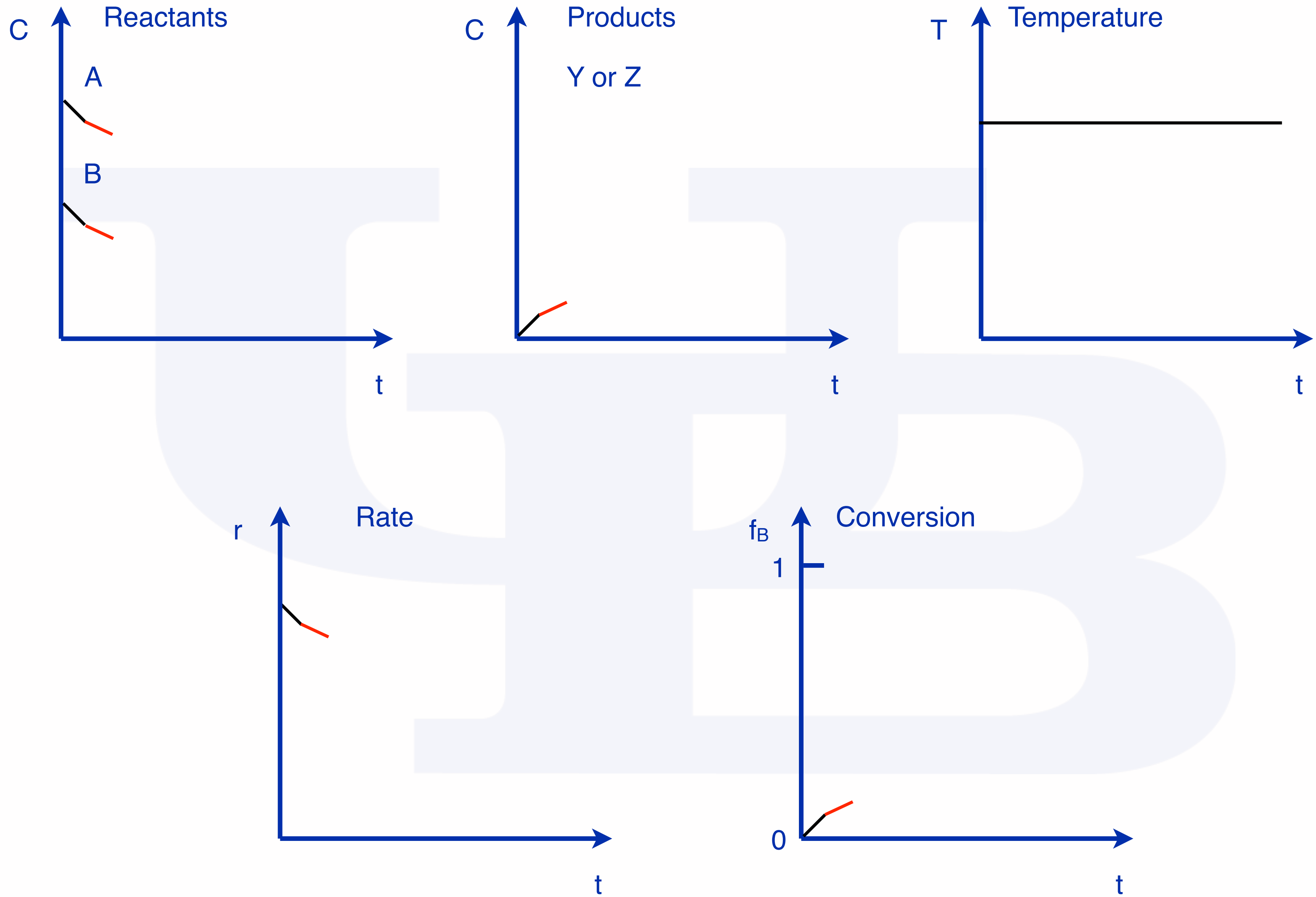

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- Determine whether continuing the initial trends will result in the rate asymptotically approaching equilibrium

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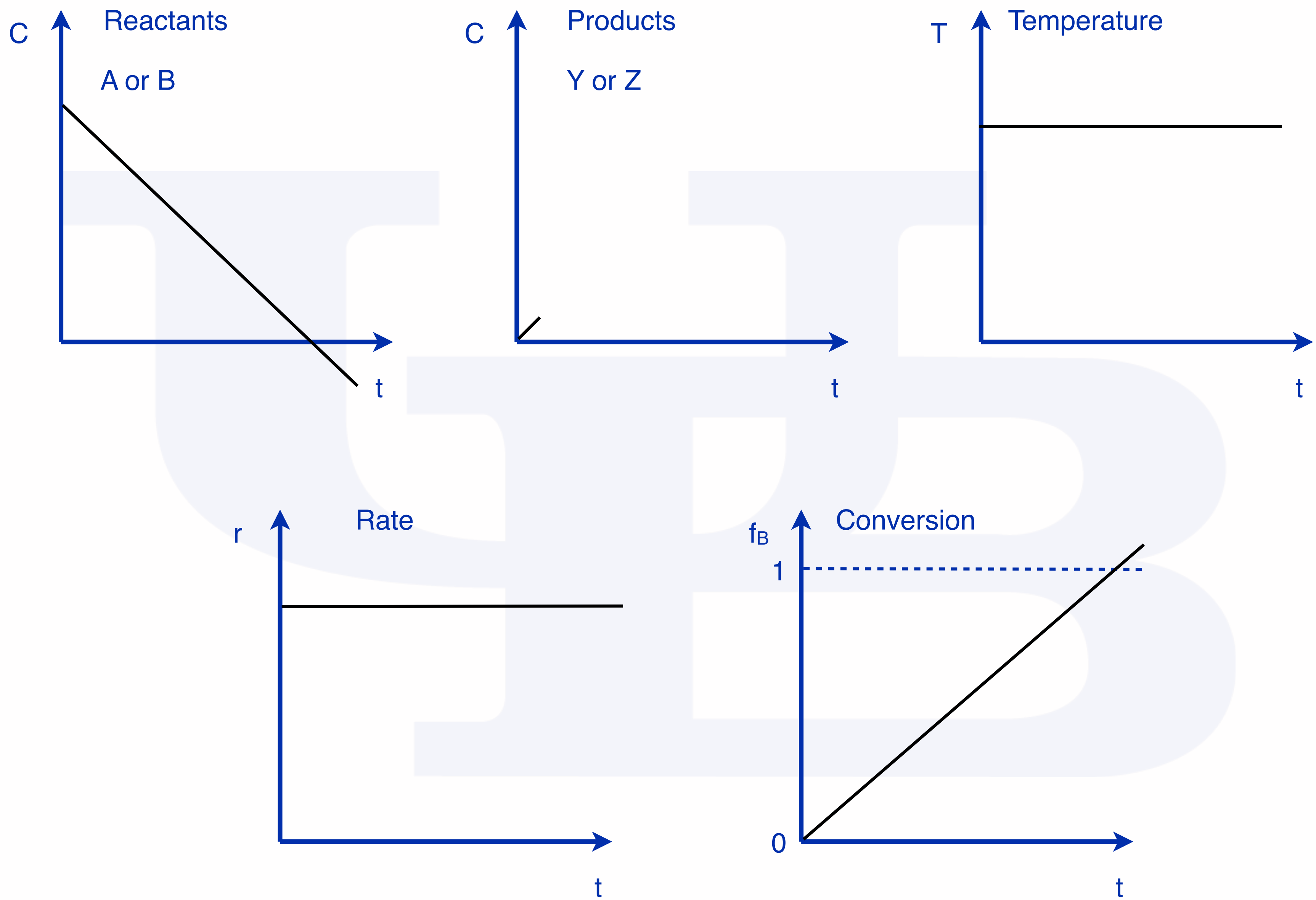
  - in case (a) the trend cannot continue, leading to equilibrium
    - reactant concentrations will become zero
    - conversion will become greater than 1
    - rate will never equal zero
  - in case (b) the trend can continue
    - concentration of B will go to zero
    - concentration of A will become constant
    - conversion will become 1
    - rate will equal zero

Case (a)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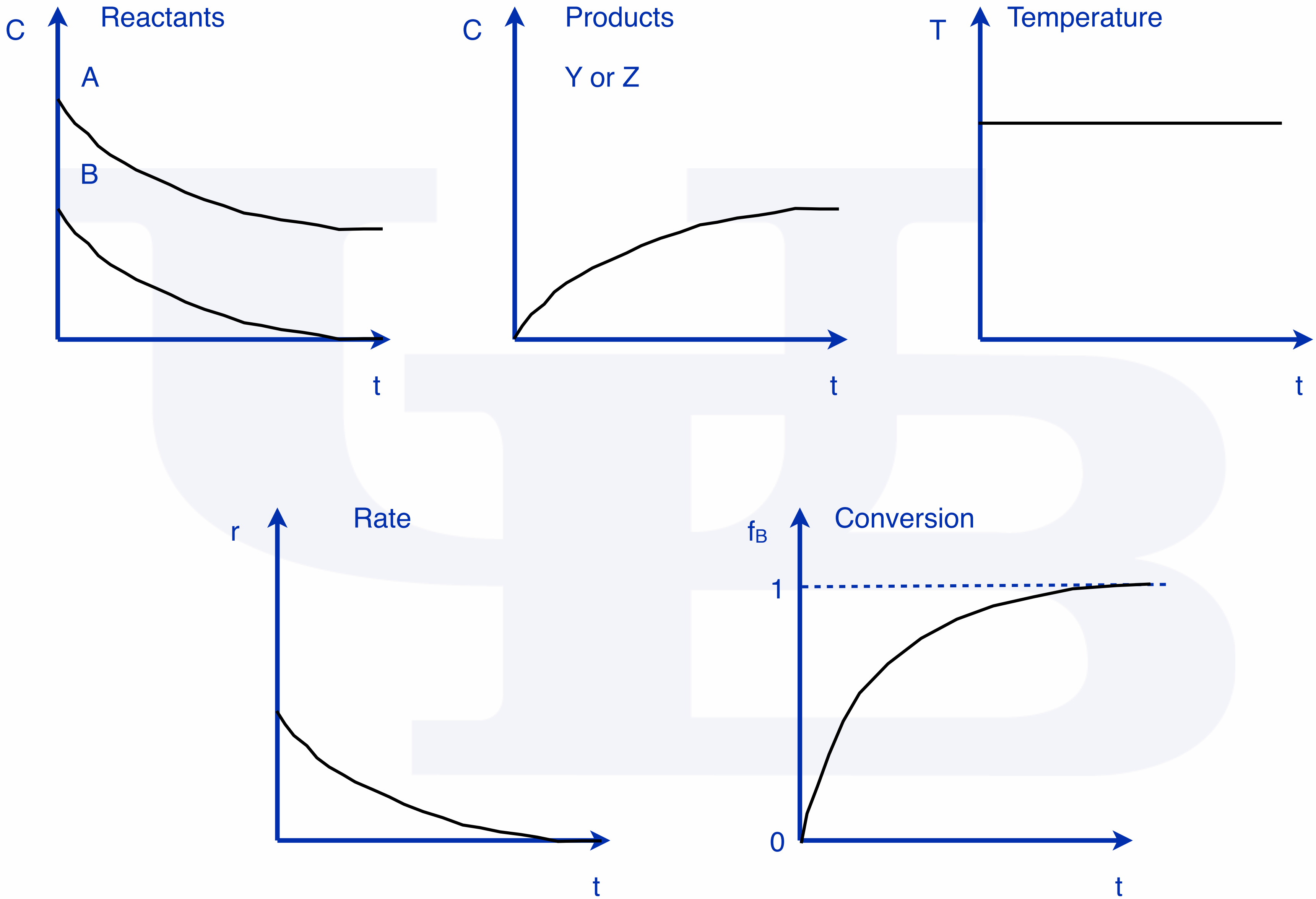

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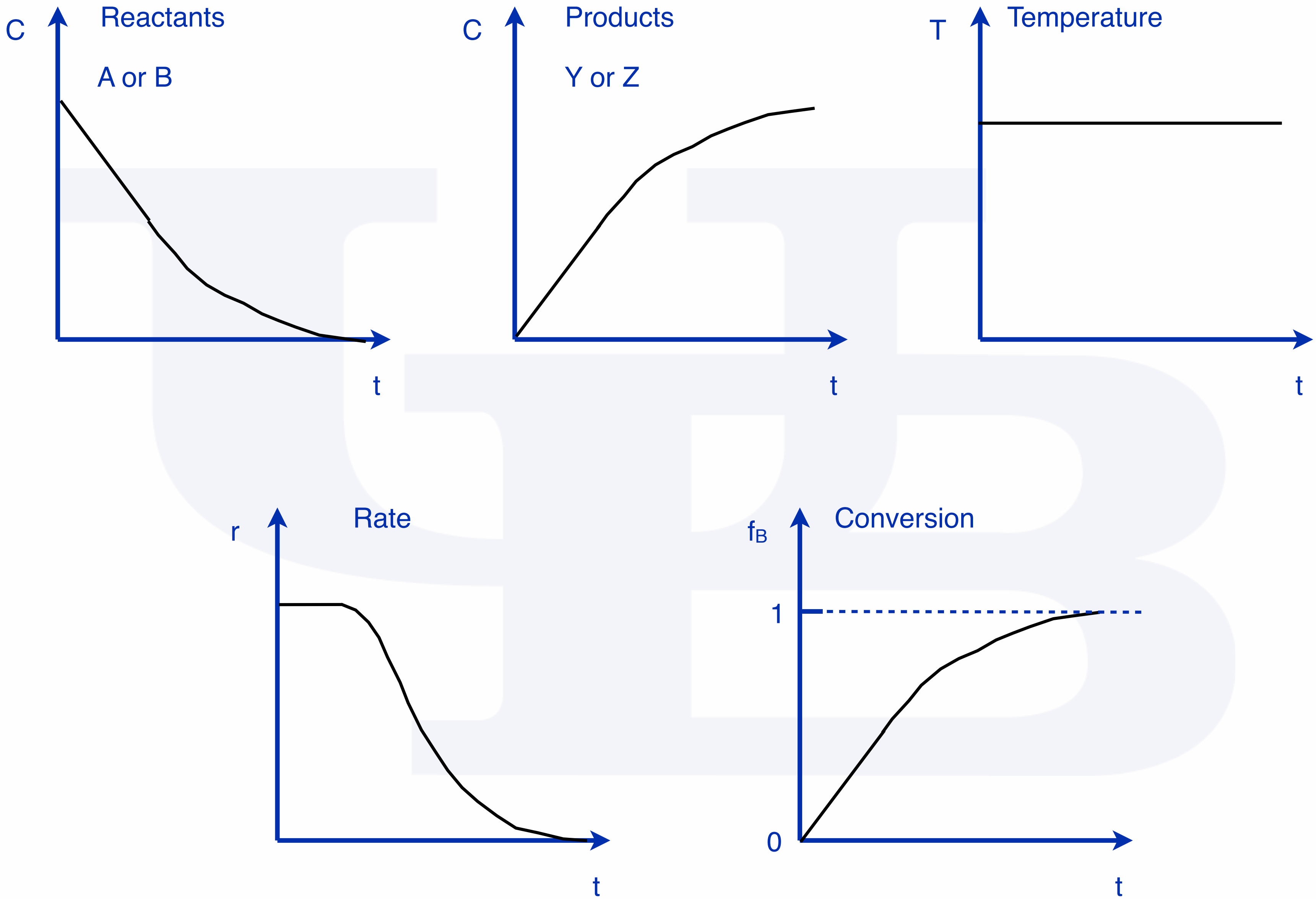
    - conversion will become greater than 1
    - rate will never equal zero
  - If not, infer what must happen so that the system approaches equilibrium properly (i. e. so the rate progressively decreases to zero) and add to the corresponding plots
    - At some point, the K in the denominator will become significant so that the numerator decreases more than the denominator and the rate will start to decrease more and more (concave up)
    - Eventually the P_A in the denominator will become negligible after which the rate will decrease less and less (inflection point then concave down)
    - During this whole time the rate is decreasing in each successive time interval; as a consequence
      - the reactant concentrations will decrease by less and less (concave up)
      - the product concentrations will increase by less and less (concave down)
      - the conversion will increase by less and less (concave down)
    - These trends can continue until equilibrium is reached
      - the rate will equal zero, the concentrations and conversion equal 1

Case (a)



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- Use the plots to answer the questions posed in the problem

Qualitative Analysis with Parallel Reactions

- Suppose irreversible, parallel reactions (1) and (2) take place isothermally in a batch reactor with kinetics as indicated. Prepare a three slide presentation that describes and qualitatively justifies approaches you might employ in order to improve the selectivity for D.

$A + S \rightarrow D$	$r = 10\ e^{-10/T}\ C_A\ C_S$	(1)
$A + S \rightarrow U$	$r = 10\ e^{-15/T}\ C_A\ (C_S)^2$	(2)

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- Instantaneous selectivity parameter: $S_{D/U} = \dfrac{r_D}{r_U} = \dfrac{10e^{-10/T}C_A C_S}{10e^{-15/T}C_A C_S^2} = \dfrac{e^{5/T}}{C_S}$
  - D is favored by
    - low temperature
    - low C_S
  - Low reaction temperature will trade off rate of conversion versus selectivity to D; use the lowest acceptable temperature
  - Low initial concentration of S will trade off conversion and time per batch versus selectivity to D
- Other approaches
  - Find a catalyst that favors production of D
  - If reaction is solution phase, find a solvent that favors production of D

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