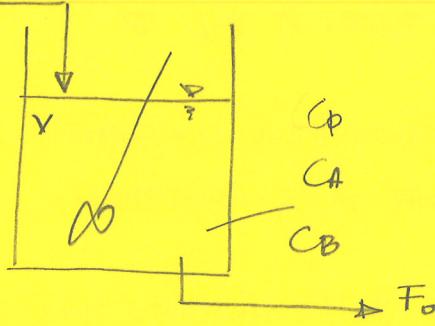


# CSTR 'first' order irreversible reaction



Assume that two chemical species A and B are in a solvent feedstream entering a liquid phase chemical reactor

- the reactor is maintained at constant temperature
- The two species react to form a third species P

WE ARE INTERESTED IN THE REACTOR CONCENTRATION AS A FUNCTION OF TIME

## Total mass balance

$$\frac{dM}{dt} = \frac{dVp_0}{dt} = F_i p_i - F_o p_o$$



$$p_i = p_o$$

$$\frac{dV}{dt} = F_i - F_o$$

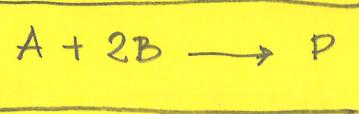
and WE CAN ASSUME THAT THE LIQUID PHASE DENSITY IS NOT A FUNCTION OF THE CONCENTRATION

$$\frac{dH}{dt} = \rho (F_i - F_o)$$

## Component mass balance

let  $C_A$ ,  $C_B$  and  $C_P$  the molar concentrations of species A, B, P

Assume the stoichiometric equation



Assuming that there is no component P in the feed, we have

$$* \frac{dVC_A}{dt} = F_i C_{Ai} - F_o C_A + Vr_A$$

$$* \frac{dVC_B}{dt} = F_i C_{Bi} - F_o C_B + Vr_B$$

$$* \frac{dVC_P}{dt} = - F_o C_P + Vr_P$$

$$F_i C_{Pi} = 0$$

$r_A$ ,  $r_B$  and  $r_P$  ARE GENERATION RATES OF SPECIES A, B AND P PER UNIT VOLUME

$C_{Ai}$  AND  $C_{Bi}$  ARE INLET CONCENTRATIONS OF A AND B

$$r_A = \frac{\text{moles of A}}{\text{volume time}}$$

WE CAN ASCRIBE THAT THE RATE OF REACTION OF A (PER UNIT VOLUME) IS 2nd ORDER AND A FUNCTION OF THE CONCENTRATION OF BOTH A AND B

$$* \quad r_A = -k C_A C_B \quad \text{where } k \text{ is the reaction rate constant}$$

(-) indicates that A is consumed

AS ONE MOLE OF A REACTS WITH TWO MOLES OF B (STOICHIOMETRIC EQ.) TO PRODUCE ONE MOLE OF P, WE HAVE

RATE OF GENERATION OF B (PER UNIT VOLUME)

$$* \quad r_B = -2k C_A C_B$$

RATE OF GENERATION OF P (PER UNIT VOLUME)

$$* \quad r_P = k C_A C_B$$

Thus, we can write

$$* \quad \frac{dV_{CA}}{dt} = V \frac{dC_A}{dt} + C_A \frac{dV}{dt} = F_i C_{Ai} - F_o C_A + V (-k C_A C_B)$$

$$\text{and } \frac{dC_A}{dt} = \frac{F_i C_{Ai} - F_o C_A - V k C_A C_B}{V} - \frac{C_A}{V} \frac{dV}{dt}$$

$$\text{WITH } \frac{dV}{dt} = F_i - F_o$$

$$\text{and } \frac{dC_A}{dt} = \frac{F_i C_{Ai}}{V} - \frac{F_o C_A}{V} - k C_A C_B - \frac{C_A}{V} F_i + \frac{C_A}{V} F_o$$

$$= F_i/V (C_{Ai} - C_A) - k C_A C_B$$

SIMILARLY FOR B AND P

$$* \quad \frac{dC_B}{dt} = \frac{F_i}{V} (C_{Bi} - C_B) - 2k C_A C_B$$

$$* \quad \frac{dC_P}{dt} = -\frac{F_i}{V} C_P + k C_A C_B$$

AND, OF COURSE, WE HAVE

$$* \quad \frac{dV}{dt} = F_i - F_o$$

The model consists of 4 first order differential eqn.  
- 4 STATE VARIABLES

To solve the equations, initial conditions must be provided  
 $V(0), C_A(0), C_B(0), C_P(0)$

AND THE INPUTS AS FUNCTIONS OF TIME

$$F_i(t), C_{Ai}(t), C_{Bi}(t)$$

The reactor model has four 1st order differential equations

$$\frac{dC_A}{dt} = \frac{F_i}{V} (C_{Ai} - C_A) - K C_A C_B$$

$$\frac{dC_B}{dt} = \frac{F_i}{V} (C_{Bi} - C_B) - 2 K C_A C_B$$

$$\frac{dC_P}{dt} = -\frac{F_i}{V} C_P + K C_A C_B$$

$$\frac{dV}{dt} = F_i - F_o$$

It is possible to formulate some simplifying assumptions to make the analysis easier

→ CONSTANT VOLUME

$$\boxed{\frac{dV}{dt} \approx 0}$$

This is THE SIMPLEST AND OFTEN MOST REALISTIC ASSUMPTION

It is also possible to assume that one of reactant is maintained in large excess, thus constant

→ IF SPECIES B IS IN LARGE EXCESS,  $C_B$  IS NEARLY CONSTANT

$$\boxed{* \frac{dC_B}{dt} \approx 0}$$

$$* \dot{t}_A = -K C_A C_B \approx -K_1 C_A \quad \text{WITH } K_1 = C_B K$$

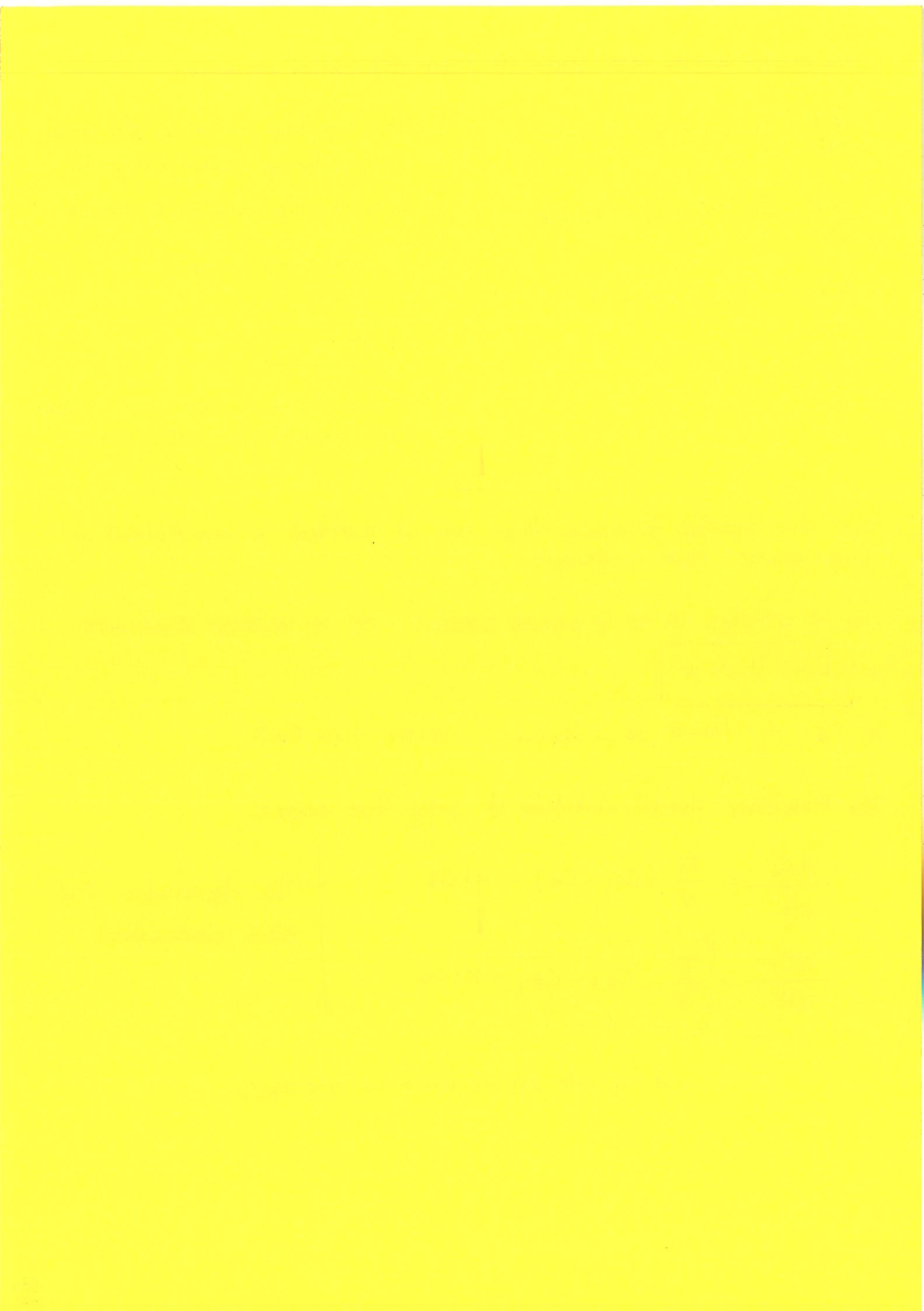
The resulting model consists of only two states

$$\frac{dC_A}{dt} = \frac{F_i}{V} (C_{Ai} - C_A) - K_1 C_A$$

$$\frac{dC_P}{dt} = \frac{F_i}{V} (C_{Pi} - C_P) + K_1 C_A$$

= 0 IF WE ASSUME NO P IN THE FEED

The dynamics of A also decoupled



Models can contain a large number of parameters and variables  
 → THERE MAY BE DIFFERENCES IN VALUE BY ORDERS OF MAGNITUDE

It is often desirable for analysis purposes to develop models consisting of dimensionless parameters and variables

CONSIDER AS AN EXAMPLE  $\frac{dC_A}{dt} = \frac{F}{V} (C_{A_i} - C_A) - k C_A$

IT SEEKS NATURAL TO CONSIDER A SCALED CONCENTRATION  $x = C_A/C_{A_0}$   
 WHERE  $C_{A_0}$  IS SOME NOTIONAL, FOR EXAMPLE STEADY STATE CONCENTR.

$$\frac{dC_A/C_{A_0}}{dt} = \frac{F}{V} \left( \frac{C_{A_i}}{C_{A_0}} - \frac{C_A}{C_{A_0}} \right) - k \frac{C_A}{C_{A_0}}$$

$$\text{and } \frac{dx}{dt} = \frac{F}{V} \left( x_i - x \right) - k x, \quad \text{with } x_i = \frac{C_{A_i}}{C_{A_0}}$$

$$= \frac{F}{V} x_i - x \left( \frac{F}{V} + k \right)$$

IT IS ALSO NATURAL TO CHOOSE A SCALED TIME  $\tau = t/t^*$   
 WITH  $t^*$  SOME PARAMETER TO BE DETERMINED

FROM  $dt = t^* d\tau$  WE HAVE

$$\frac{dx}{d\tau \cdot t^*} = \frac{F}{V} x_i - x \left( \frac{F}{V} + k \right)$$

THAT IS  $\frac{dx}{d\tau} = \frac{F}{V} t x_i - x t \left( \frac{F}{V} + k \right)$

Damkohler number

IF WE LET  $t$  BE  $\frac{V}{F}$ , WE CAN WRITE  $\frac{dx}{dt} = x_i - x \left( 1 + \underbrace{k \frac{V}{F}}_{\alpha} \right)$

Assuming that the feed concentration is maintained constant  $x_f = 1$   
 and letting  $\alpha = VK/F$ , we have

$$\frac{dx}{dt} = 1 - x + \alpha x$$

↑  
a single parameter



CONSIDER THE MODELLING EQUATIONS

$$\frac{dv}{dt} = F_i - F_o$$

$$\frac{dC_A}{dt} = \frac{F_i}{V} (C_{A_i} - C_A) - K C_A C_B$$

$$\frac{dC_B}{dt} = \frac{F_i}{V} (C_{B_i} - C_B) - 2 K C_A C_B$$

$$\frac{dC_P}{dt} = -\frac{F_i}{V} C_P - K C_A C_B$$

- WE HAVE 4 STATE VARIABLES

$$x = [v, C_A, C_B, C_P]$$

- WE HAVE 4 INPUT VARIABLES

$$u = [F_i, F_o, C_{A_i}, C_{B_i}]$$

- 1 PARAMETER  $\theta = [K]$

WE CAN WRITE

$$\begin{bmatrix} v \\ C_A \\ C_B \\ C_P \end{bmatrix} = \begin{bmatrix} F_i - F_o \\ F_i/V(C_{A_i} - C_A) - K C_A C_B \\ F_i/V(C_{B_i} - C_B) - 2 K C_A C_B \\ -F_i/V C_P + K C_A C_B \end{bmatrix} \quad \text{OR}$$

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \\ \dot{x}_4 \end{bmatrix} = \begin{bmatrix} u_1 - u_2 \\ u_1/x_1 (u_3 - x_2) - p_1 x_2 x_3 \\ u_1/x_1 (u_4 - x_3) - 2 p_1 x_2 x_3 \\ -u_1/x_1 (x_4) + p_1 x_2 x_3 \end{bmatrix} = \begin{bmatrix} f_1(x, u | p) \\ f_2(x, u | p) \\ f_3(x, u | p) \\ f_4(x, u | p) \end{bmatrix}$$



$$\begin{aligned} \frac{dx_1 - x_s}{dt} &= \begin{bmatrix} \partial f_1 / \partial x_1|_{ss} & \partial f_1 / \partial x_2|_{ss} & \dots & \partial f_1 / \partial x_n|_{ss} \\ \partial f_2 / \partial x_1|_{ss} & \partial f_2 / \partial x_2|_{ss} & \dots & \partial f_2 / \partial x_n|_{ss} \\ \vdots & \vdots & \ddots & \vdots \\ \partial f_n / \partial x_1 & \end{bmatrix} \\ \frac{dx_2 - x_s}{dt} &= \\ \vdots & \\ \frac{dx_n - x_s}{dt} &= \end{aligned}$$

$$\frac{\partial f_1}{\partial x_1} = 0 \quad * \quad \frac{\partial f_1}{\partial x_2} = 0 \quad * \quad \frac{\partial f_1}{\partial x_3} = 0 \quad * \quad \frac{\partial f_1}{\partial x_n} = 0$$

$$\frac{\partial f_2}{\partial x_1} = -\frac{u_1(u_3 - x_2)}{x_1^2} \quad * \quad \frac{\partial f_2}{\partial x_2} = -\frac{u_1}{x_1} - p_1 x_3 \quad * \quad \frac{\partial f_2}{\partial x_3} = -p_1 x_2 \quad * \quad \frac{\partial f_2}{\partial x_n} = 0$$

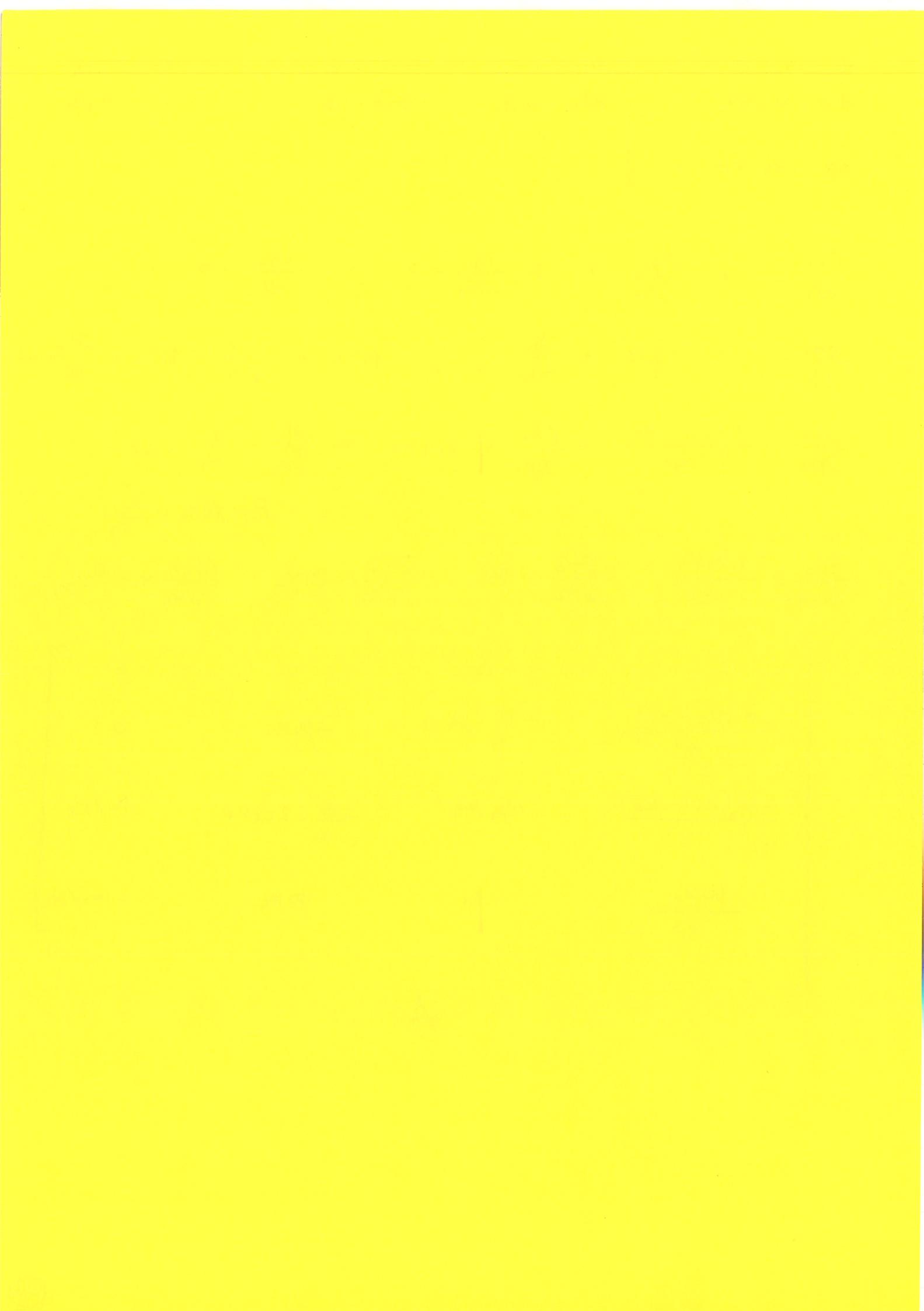
$$\frac{\partial f_3}{\partial x_1} = -\frac{u_1(u_n - x_2)}{x_1^2} \quad * \quad \frac{\partial f_3}{\partial x_2} = -2p_1 x_2 \quad * \quad \frac{\partial f_3}{\partial x_3} = -\frac{u_1}{x_1} - 2p_1 x_2$$

$$\frac{\partial f_3}{\partial x_n} = \frac{u_1}{x_1}$$

$$\frac{\partial f_n}{\partial x_1} = \frac{+u_1 x_1}{x_1^2} \quad \frac{\partial f_n}{\partial x_2} = p_1 \quad \frac{\partial f_n}{\partial x_3} = p_1 x_2 \quad \frac{\partial f_n}{\partial x_n} = -\frac{u_1}{x_1}$$

$$\begin{bmatrix} 0 & 0 & 0 & 0 \\ -\frac{u_1(u_3 - x_2)}{x_1^2} & -\frac{u_1}{x_1} - p_1 x_3 & -p_1 x_2 & 0 \\ -\frac{u_1(u_n - x_2)}{x_1^2} & -2p_1 x_2 & -\frac{u_1}{x_1} - 2p_1 x_2 & \frac{u_1}{x_1} \\ \frac{u_1 x_1}{x_1^2} & p_1 & p_1 x_2 & -\frac{u_1}{x_1} \end{bmatrix}$$

A



$$\frac{\partial f_1}{\partial u_1} = 1 \quad \frac{\partial f_1}{\partial u_2} = -1 \quad \frac{\partial f_1}{\partial u_3} = 0 \quad \frac{\partial f_1}{\partial u_4} = 0$$

$$\frac{\partial f_2}{\partial u_1} = \frac{1}{x_1}(u_2 - x_2) \quad \frac{\partial f_2}{\partial u_2} = 0 \quad \frac{\partial f_2}{\partial u_3} = \frac{u_1}{x_1} \quad \frac{\partial f_2}{\partial u_4} = 0$$

$$\frac{\partial f_3}{\partial u_1} = \frac{1}{x_1}(u_3 - x_3) \quad \frac{\partial f_3}{\partial u_2} = 0 \quad \frac{\partial f_3}{\partial u_3} = 0 \quad \frac{\partial f_3}{\partial u_4} = \frac{u_1}{x_1}$$

$$\frac{\partial f_4}{\partial u_1} = -\frac{x_4}{x_1} \quad \frac{\partial f_4}{\partial u_2} = 0 \quad \frac{\partial f_4}{\partial u_3} = 0 \quad \frac{\partial f_4}{\partial u_4} = 0$$

$$\begin{bmatrix} 1 & -1 & 0 & 0 \\ \frac{1}{x_1}(u_2 - x_2) & 0 & u_1/x_1 & 0 \\ \frac{1}{x_1}(u_3 - x_3) & 0 & 0 & u_1/x_1 \\ -\frac{x_4}{x_1} & 0 & 0 & 0 \end{bmatrix}$$

B

$$\underbrace{\begin{bmatrix} d(x_1 - x_1^s)/dt \\ d(x_2 - x_2^s)/dt \\ d(x_3 - x_3^s)/dt \\ d(x_4 - x_4^s)/dt \end{bmatrix}}_{\dot{x}^s} = A \underbrace{\begin{bmatrix} x_1 - x_1^s \\ x_2 - x_2^s \\ x_3 - x_3^s \\ x_4 - x_4^s \end{bmatrix}}_{x^s} + B \begin{bmatrix} m_1 - m_1^s \\ m_2 - m_2^s \\ m_3 - m_3^s \\ m_4 - m_4^s \end{bmatrix}$$

