1. Mass Balance for a Mixture with Chemical Reaction

   At high temperatures acetaldehyde (CH_3CHO) dissociates into methane and carbon monoxide by the following reaction

   $$CH_3CHO \rightarrow CH_4 + CO$$

   At 520°C the rate at which acetaldehyde dissociates is

   $$\frac{dC_{CH_3CHO}}{dt} = -0.48C^2_{CH_3CHO}\frac{m^3}{kmol\ s}$$

   where C is the concentration in kmol/m³. The reaction occurs in a constnt-volume, 1-L vessel, and the initial concentration of acetaldehyde is 10 kmol/m³

   a. If 5 mols of the acetaldehyde reacts, how much methane and carbon monoxide is produced?

First identify ν_B (the stoichiometric coefficient) for each species.

$CH_3CHO \rightarrow CH_4 + CO$ is rearranged to $CH_4 + CO - CH_3CHO = 0$

From that form the stoichiometric coefficient is readily identifiable

$\nu_{CH4} = +1$ $\qquad$ $\nu_{CO} = +1$ $\qquad$ $\nu_{CH3CHO} = -1$

at this point expressions for their present value can be obtained using the form:

$N_{a,i} = N_{a,o} + V_a \bullet X$

where $N_{a,i}$ is the quantity of species a @ time t	V_a is the stoichiometric coefficient of species a
$N_{a,0}$ is the quantity of species a @ time 0	X is the extent of reaction.

Specifically we get the following expressions

$N_{CH3CHO} = 10 - X$ $\qquad$ $N_{CH4} = X$ $\qquad$ $N_{CHO} = X$

A) 5 mols of CH_3CHO is used, this means X = 5. Using the above equations

   $N_{CH3CHO} = 10 - X$ $\qquad$ $N_{CH4} = X$ $\qquad$ $N_{CHO} = X$

   $N_{CH3CHO} = 5mols$ $\qquad$ $N_{CH4} = 5mols$ $\qquad$ $N_{CHO} = 5mols$

B) Develop expressions for the amounts of acetaldehyde, methane, and carbon monoxide present at any time, and determine how long it would take for 5 mol of acetaldehyde to have reacted.

The first part of the question asks for expressions for each species at any time. These expressions were formulated above.

$N_{CH3CHO} = 10 - X$ $\qquad$ $N_{CH4} = X$ $\qquad$ $N_{CHO} = X$

X is the extent of reaction at time t. you can substitute from the latter half of this problem to put each species in terms of time directly.

The 2nd part wants the time for 5 mol acetaldehyde to have reacted.

The problem provides a rate law for acetaldehyde

$$\frac{dC_{CH3CHO}}{dt} = -.48C_{CH3CHO}^2$$

C is concentration.

The question asks for time. So you can integrate to introduce a variable T and then solve for T. There are many ways to do this. I will demonstrate what we feel is the simplest.

First how can you relate C_{CH3CHO} to N_{CH3CHO}?

C = N/V or in this case $C_{CH3CHO} = N_{CH3CHO}$ / Volume

Because we have information about mols of CH_3CHO being used – lets use that form (you could instead convert the expression we have into Concentration if you insisted)

If we substitute as appropriate we find that the rate law becomes

$$\frac{dC_{CH3CHO}}{dt} = -.48C_{CH3CHO}^2 \quad \rightarrow \quad \frac{d\,N_{CH3CHO}/Volume}{dt} = -.48\,\frac{N_{CH3CHO}^2}{Volume^2}$$

Let's rearrange so that we have some components we're familiar with.

$$\frac{1}{Volume}\frac{dN_{CH3CHO}}{dt} = -.48\,\frac{N_{CH3CHO}^2}{Volume^2}$$

Hopefully you can recognize that earlier we determined $N_{CH3CHO} = 10 - X$

$$\frac{1}{Volume}\frac{dN_{CH3CHO}}{dt} = -.48\,\frac{(10-X)^2}{Volume^2}$$

The first "tricky" part we've got to get rid of the dN_{CH3CHO}.

Strategy #1 Theory based substitution

dN_{CH3CHO}/dt is **by definition** the rate of change of N_{CH3CHO} over time. How can we get that in terms of X to make this equation solvable?

Recall that $N_{a,i} = N_{a,o} + V_a \bullet X$ gives us quantity of N_a at any given time.

If you have a formula for a species at time T you can take the derivative to obtain the rate of change of that species over time.

$$N_{a,i} = N_{a,o} + V_a \bullet X \rightarrow dN/dt = V_a\,(dx/dt)$$

$$\downarrow$$

$$dN_{CH3CHO}/dt = V_{CH3CHO}\,(dx/dt)$$

If you take that substitution into the equation you get

$$\frac{1}{Vol.}\frac{dN_{CH3CHO}}{dt} = -.48\,\frac{(10-X)^2}{Volume^2} \rightarrow \frac{1}{Vol.}\mathrm{V}_{CH3CHO}\frac{dX}{dt} = -.48\,\frac{(10-X)^2}{Volume^2}$$

Now let's plug in: V_{CH3CHO} = -1 and Volume = 1 L

$$-\frac{dX}{dt} = -.48\,(10-X)^2$$

From here its just math.

Strategy #2 Plug and chug

$$\frac{1}{Volume}\frac{dN_{CH3CHO}}{dt} = -.48\,\frac{(10-X)^2}{Volume^2}$$

To get rid of the dN_{CH3CHO} just plug in 10-X again.

$$\frac{1}{Volume}\frac{d(10-X)}{dt} = -.48\,\frac{(10-X)^2}{Volume^2}$$

You can't just divide (10-X) to get rid of it in the numerator of the left side of the equation.

You have to take the derivative of d(10-X) → -dx

$$\frac{1}{Vol.}\frac{-dx}{dt} = -.48\,\frac{(10-X)^2}{Volume^2}$$

Input Volume = 1L and you get

$$-\frac{dX}{dt} = -.48\,(10-X)^2$$

And it's just math from here

MATH:

$$-\frac{dX}{dt} = -.48\,(10-X)^2 \rightarrow -\frac{1}{(10-X)^2}\frac{dX}{dt} = -.48$$

$$-\frac{1}{(10-X)^2}\frac{dX}{dt} = -.48 \quad \rightarrow \quad \frac{1}{(10-X)^2}dx = .48dt$$

Now we integrate. We have to take the definite integral of Molar extent at time 0 to time t

$$\int_{X(0)}^{X(t)} \frac{1}{(10-X)^2}dx = \int_0^t .48dt$$

So this results in $\frac{1}{10-X}\Big|_0^{X(t)} = .48t\,\Big|_0^t$

$$\frac{1}{(10-X(t))} - \frac{1}{(10-0)} = .48t - .48(0)$$

X(t) for the t we are interested in is = 5 mols so plug that in

$$\frac{1}{(10-5)} - \frac{1}{(10)} = .48t$$

So **t = 0.208**

2. At high temperatures phosphine (PH_3) dissociates into phosphorus and hydrogen by the following reaction:

$$4PH_3 \rightarrow P_4 + 6H_2$$

At 800°C the rate at which phosphine dissociates is

$$\frac{dC_{PH_3}}{dt} = -3.715\times10^{-6}\,C_{PH_3}$$

for t in seconds. The reaction occurs in a constant-volume, 2-L vessel, and the initial concentration of phosphine is 5kmol/m³

a. If 3mol of the phosphine reacts, how much phosphorus and hydrogen is produced?

$4PH_3 \rightarrow P_4 + 6H_2 \quad \Rightarrow \quad P_4 + 6H_2 - 4PH_3 = 0$

$\nu_{PH3} = -4 \quad \nu_{P4} = +1 \quad \nu_{H2} = +6$

$N_{PH3,o} = 5\ kmol/m^3 \bullet 2\ L = 10\ Mol$

$N_{PH3} = 10 - 4X \quad N_{P4} = X \quad N_{H2} = 6X$

A) To find how much P4 and H are produced find the molar extent of rxn so you can use the above expressions.

$N_{PH3} = 10 - 4X$ 3 mols are used at the time you are interested in so plug in 7 for your final amount

$7 = 10 - 4X \quad \Rightarrow \quad X = 0.75$

$N_{P4} = X = 0.75$ mols

$N_{H2} = 6X = 4.5$ mols

b. Develop expressions for the number of moles of phosphine, phosphorus, and hydrogen present at any time, and determine how long it would take for 3 mol of phosphine to have reacted.

B) The question gives you rate of change of phosphine in terms of concentration.

$$\frac{dC_{PH3}}{dt} = -3.715 \times 10^{-6} C_{PH3}$$

Rearrange this in terms of mols so you can use the equation you have for molar extent

$$C_{PH3} = N_{PH3}/Volume = \frac{10-4X}{2L}$$

Substitute back into the given rate

$$d\left(\frac{10-4X}{2}\right)/dt = -3.715 \times 10^{-6}\left(\frac{10-4X}{2}\right)$$

Use either approach explained in question 1

$$-2\frac{dX}{dt} = -3.75 \times 10^{-6}(5-2X)$$

Integrate from the 2 relevant timepoints: when X is 0 (the starting point) and when X =0.75 (the t you are interested in.

$$\int_{X(0)}^{X(t)} \frac{2}{5-2X} dX = 3.75 \times 10^{-6} dt$$

$-\log(5-2X)|_0^{.75}$= $(3.75 \times 10^{-6})t$

$\mathbf{t = 96000\ seconds}$

3. The following reaction occurs in air:

$2NO + O_2 \rightarrow 2NO_2$

at 20°C the rate of this reaction is

$$\frac{dC_{NO}}{dt} = -1.4\times10^{-4}\, C_{NO}^2 C_{O_2}$$

for t in seconds and concentrations in kmol/m³. The reaction occurs in a constant-volume, 2-L vessel, and the initial concentration of NO is 1kmol/m³ and that of O_2 is 3kmol/m³

a. If 0.5 mol of NO reacts, how much NO_2 is produced?

$2NO + O_2 \rightarrow 2NO_2 \Rightarrow$ $2NO_2 - O_2 - 2NO = 0$

$\nu_{NO} = -2$ $\nu_{O2} = -1$ $\nu_{NO2} = 2$

Convert given concentrations to mols to find initial conditions

N_{NO} = 2-2X N_{O2} = 6 - X N_{NO2} = 2X

If 0.5 mol of NO has reacted then then 1.5 mol of NO remain. To find molar extent of reaction

1.5 = 2 – 2X so X = 0.25

thus N**O_2 = 0.5 mol**

b. Determine how long it would take for 0.5 mol of NO to have reacted.

$$\frac{dC_{NO}}{dt} = -1.4 \times 10^{-4} C_{NO}^2 C_{O2}$$

$$C_{NO} = \frac{N_{NO}}{Vol} = \frac{2 - 2X}{2} = 1 - X$$

$$C_{O2} = \frac{N_{O2}}{Vol} = \frac{6 - X}{2}$$

$$\frac{dC_{NO}}{dt} = -1.4 \times 10^{-4} C_{NO}^2 C_{O2} \Rightarrow \frac{d(1 - X)}{dt} = -1.4 \times 10^{-4} (1 - X)^2 \frac{6 - X}{2}$$

$$\frac{-dX}{dt} = -1.4 \times 10^{-4} (1 - X)^2 \frac{6 - X}{2}$$

$$\int_{X(0)}^{X(t)} \frac{1}{(1 - X)^2 \left(\frac{6 - X}{2}\right)} dX = 1.4 \times 10^{-4} dt$$

The relevant X(t) is X(t) = 0.25

The integral is very complicated. They will be simpler on the exam.

$$\frac{2}{25} \left(\frac{5}{X - 1} + \log(6 - X) - \log(X - 1) \right) |_0^{.25} = .00014t$$

t=812.311