## 3. Kinetics of a reaction involving D-ribose 5 Phosphate

Ribose 5-phosphate (R5P) plays an important role as the starting molecule for the synthesis of purine and pyrimidine nucleotides. As such its reactions have received considerable study. Sanwick et al (2005) measured reaction rates for R5P and glycine (GLY) in a Maillard reaction (more commonly of food flavor fame!).
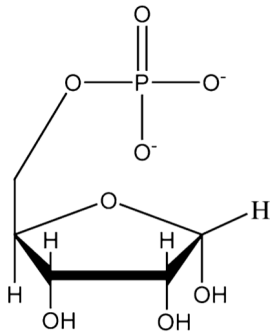
The reaction rate expression is listed (consistent with 1 to 1 stoichiometry) as

Rate = k [GLY] [R5P]

UV Absorbance at 280 nm is used to track the concentration of a (consistent with the Maillard reaction...) "brownish" product. The 280nm light is likely absorbed by an aromatic ring.

time (hr)	(initial glycine) .1M	c/c0	(initial glycine) 0.05M	c/c0
0		1		1
1		0.31622777		0.39810717
5		0.03981072		0.17782794
10		0.00125893		0.03981072
19		0.0000001		0.00050119

A. From the 1st c/c0 data, is this reaction 2nd order in the stoichiometric relation, or can you model it as first order?

B. What k values would you get for the two different possibilities?

C. Now consider the 2nd column of data, do the two columns of data give consistent results?

D. Find an algebraic expression for the concentration of R5P as a function of time in a batch reactor if the initial concentration is C_0.

E. Using the "best" first order rate constant from the first column of data, at what time is the concentration down to 2% of its initial concentration.

You may have heard that *Remdesivir* has received some level of approval for treatment of COVID-19. A big problem is that it is hard to make and very little of it is available at the moment. The connection to this exam question is tenuous, except that *Remdesivir* can be synthesized starting with ribose derivatives.

Even though we might wish to have large amount of this compound it is not clear that continuous processing in a CFSTR would be feasible.

Thus consider just a first order reaction, $A \longrightarrow M$ in a CFSTR.

F. Find an expression for C_A, concentration of A in terms of V, the volume of the reactor, k the first order rate constant and q, the feed volumetric flow rate.

G. Define the residence time, $\theta = V/q$. Find an expression for the exit A concentration C_A in terms of the feed A concentration, C_{Af} in terms of residence time and any other needed variables.

H. By comparing this exit to feed ratio for the batch reactor and the CFSTR, show that a batch reactor will always have a smaller ratio at the same "time" either batch time or resistance time.

I. Explain why this is the case.

3) LOOKS 1ST ORDER IN

1⊖   a c/c_0 ...

$$-k = .83 \qquad h = \underline{100}$$

5 b)

5 c) $k = -.38$

5 d) ~ NOT REALLY

e) $$\frac{dC_A}{dt} = -k C_A$$

$$C_A = C_{A_0} exp(-kt)$$
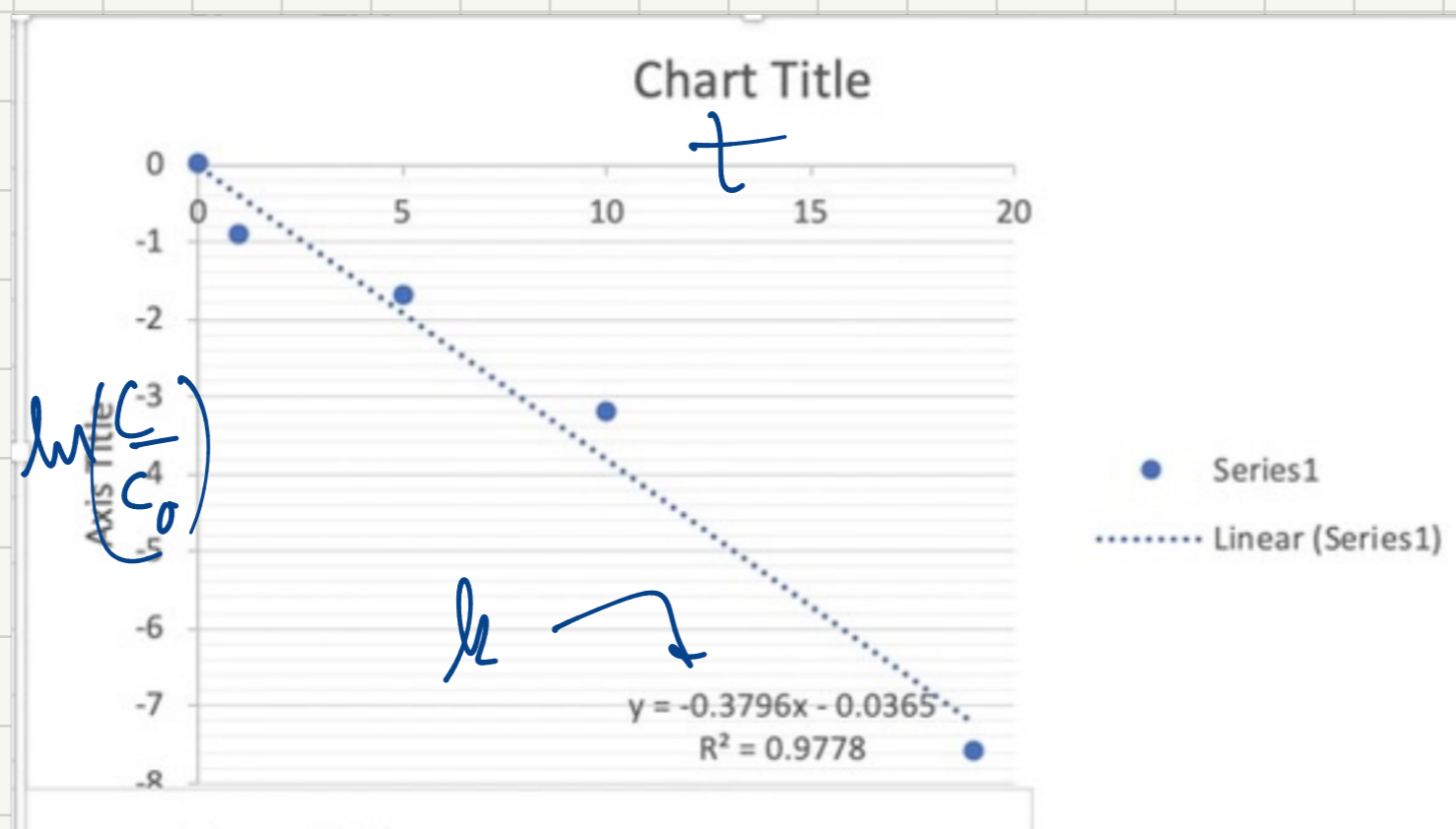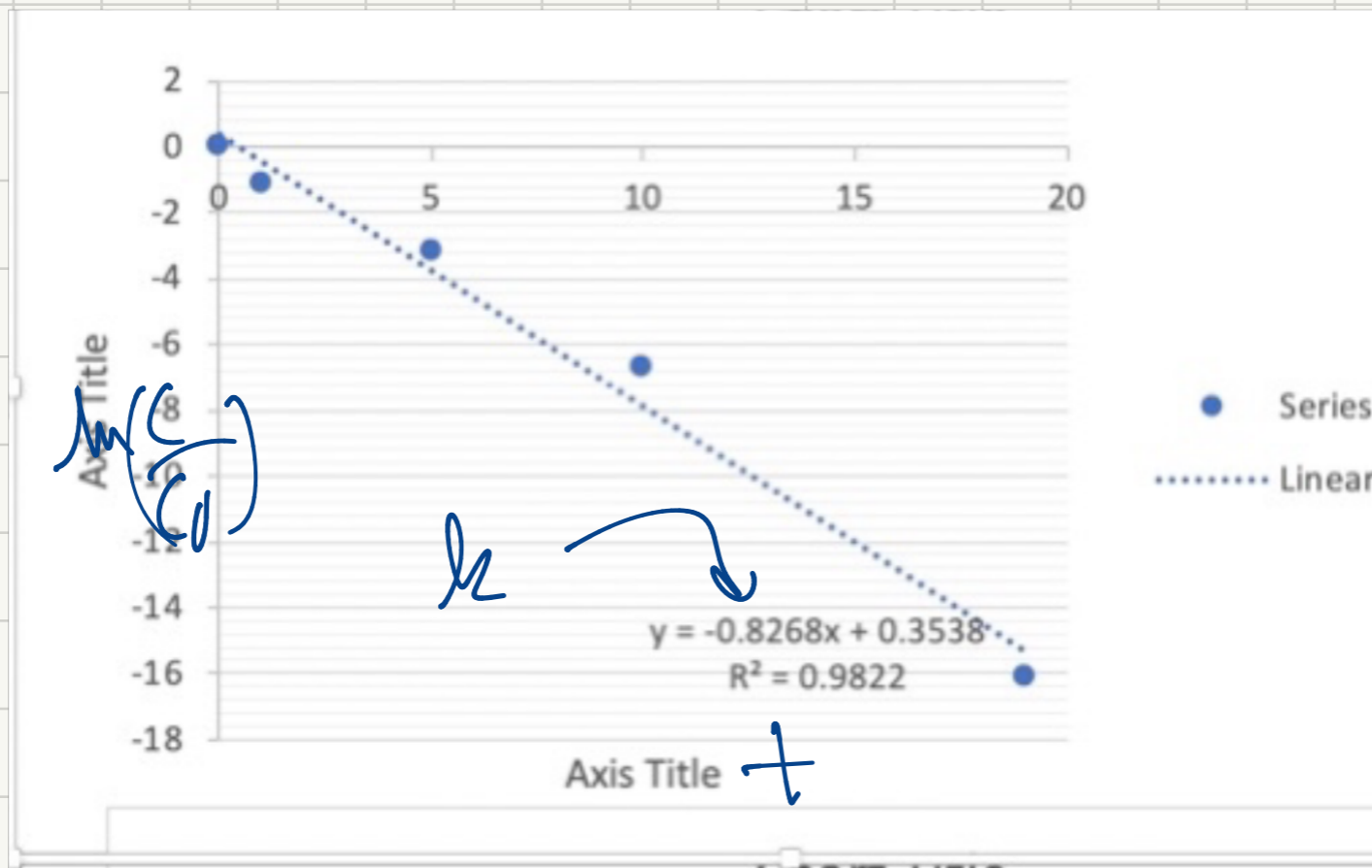
2) $$ln(.02) = -kt$$

$$t = \cdot \frac{ln(.02)}{.83} = 4.7 \, hr$$

5)

$$t = -\frac{ln}{.38} = 10 \, hr$$

3) THE TWO 1ST ORDER DATA PLOTS ARE:

THESE LOOK OK, EVEN IF k IS DIFFERENT.

THE 2ND, 2ND ORDER PLOT IS

a) ONLY 1ST ORDER LOOKS OK.

b) $.83/hr$, - 1ST ORDER

c) $.38/hr$ - 1ST ORDER

ACTUALLY IF WE WERE "HACKING"
2ND ORDER TO PSEUDO-FIRST ORDER

$$k_2' = C_0 k$$

↑

THE C_0 CHANGES BY A
FACTOR OF 2. SO
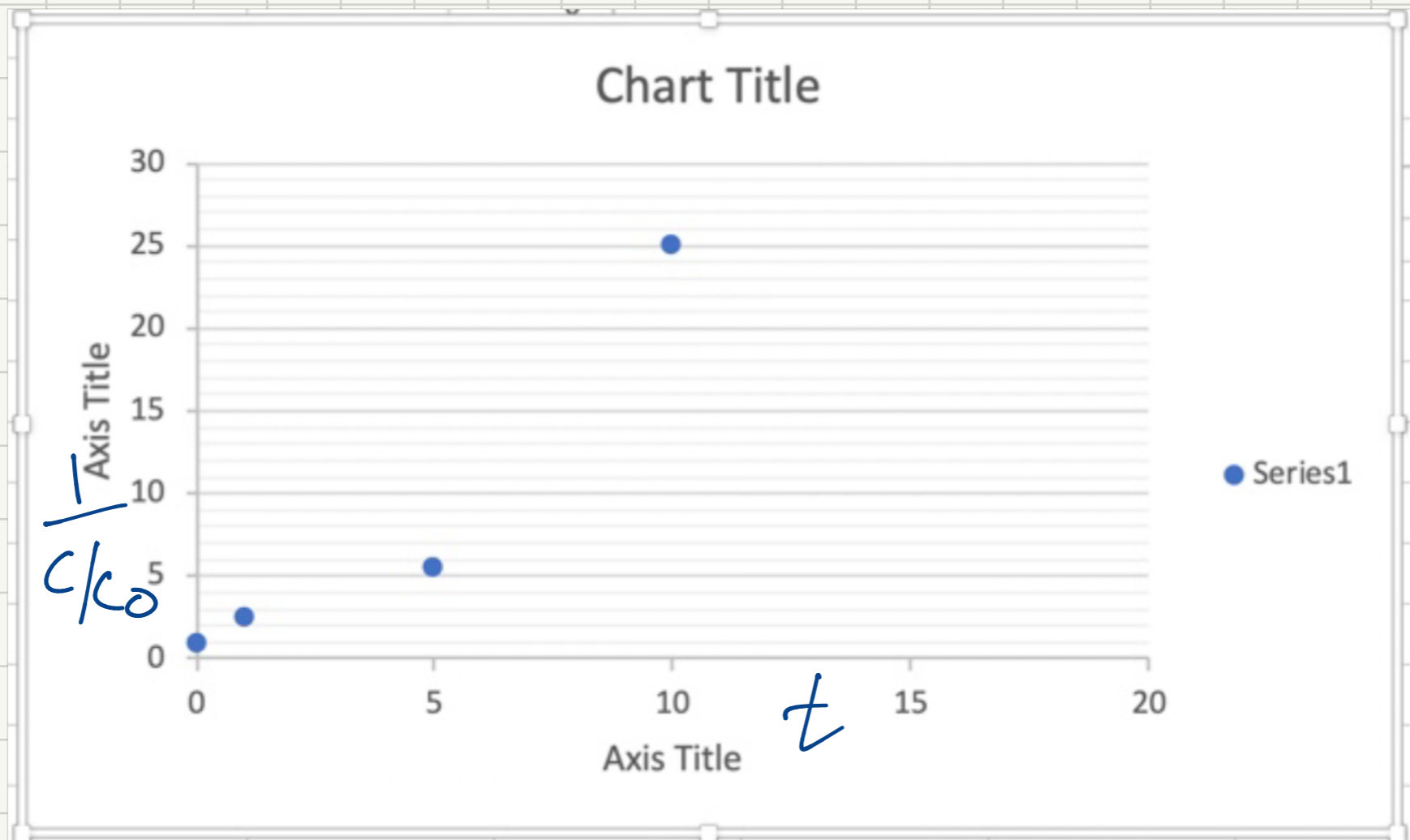$.83 \implies .38$ ARE
NOT THAT DIFFERENT.

d) $\frac{dC_A}{dt} = -k C_A$

$$C_A = C_{A_0} \exp(-kt)$$

e) $\ln(.02) = -kt$

$$t = -\frac{\ln(.02)}{.83} = 4.7 \, hr$$

Chart Title

$\frac{1}{C/C_0}$ (Axis Title)

t (Axis Title)

• Series1

1 SUPPOSE A RATE CONSTANT COULD BE OBTAINED, BUT THE FIRST DATA SET IS NOT GOOD.
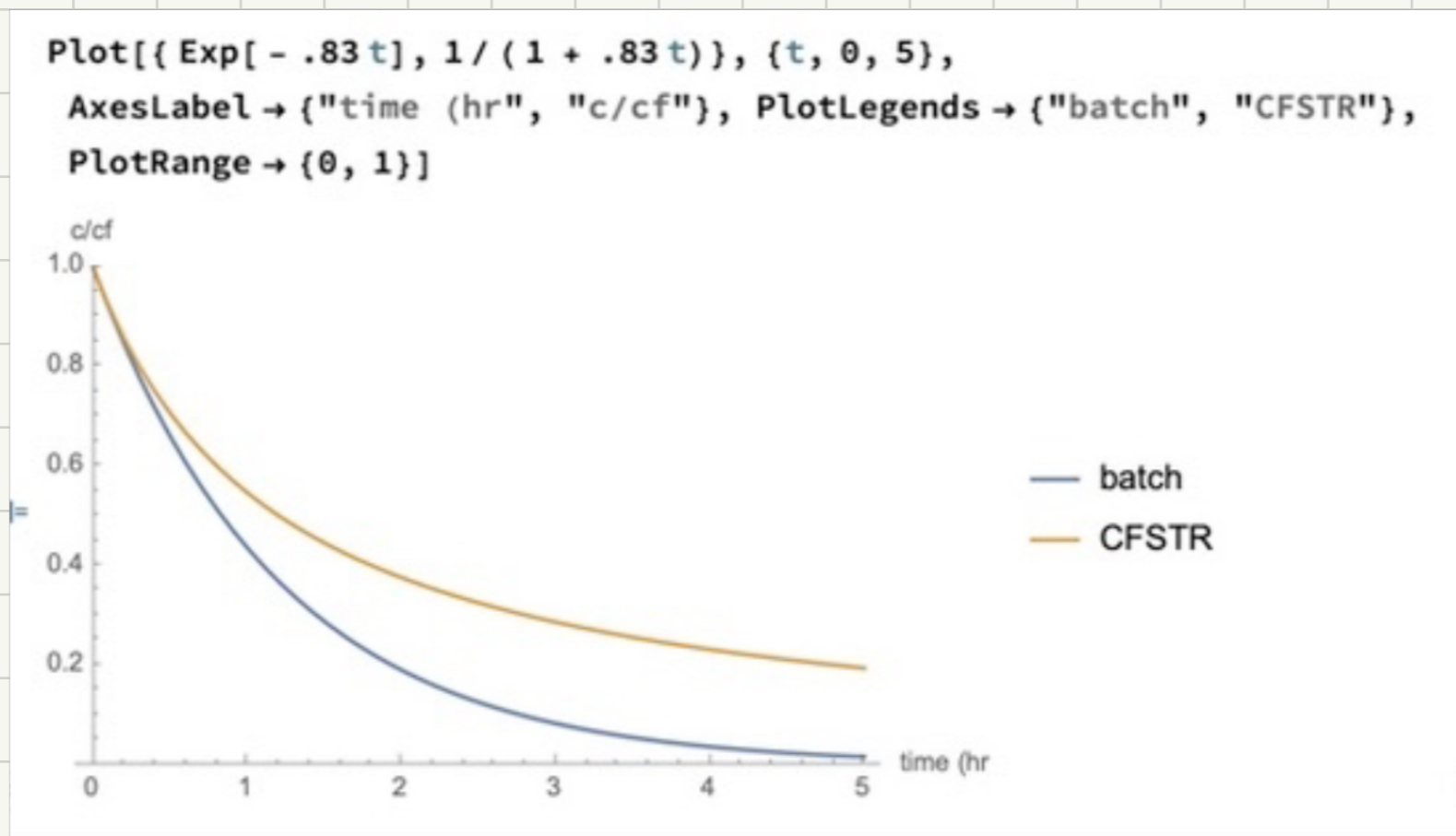
• → 1ST ORDER IS BEST.

f)
$$0 = q_{Af} C_{Af} - q C_A - - k C_A V$$

$$\frac{C_A}{C_{Af}} = \frac{1}{1 + k V/q}$$

g)
$$\frac{C_A}{C_{Af}} = \frac{1}{1 + k\theta} \qquad CFSTR$$

$$\frac{C}{C_{Ac}} = exp(-kt) \qquad BATCH$$

h)

```
Plot[{ Exp[ - .83 t], 1 / ( 1 + .83 t)}, {t, 0, 5},
 AxesLabel → {"time (hr", "c/cf"}, PlotLegends → {"batch", "CFSTR"},
 PlotRange → {0, 1}]
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i) CFSTR RATE IS AT EXIT CONCENTRATION, THE LOWEST POSSIBLE VALUE. BATCH IS ALWAYS ABOVE THIS...

Formulae:
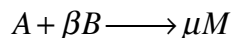
$$\frac{d\rho V}{dt} = \dot{m}_{in} - \dot{m}_{out}$$

$$V\frac{dc}{dt} = qc_{in} - qc + S - D$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$-\int_{C_{A0}}^{C_A} \frac{1}{\xi^2}d\xi = \frac{1}{C_A} - \frac{1}{C_{A0}}$$

$$\int_{x_0}^{x} \frac{1}{(\xi - \alpha)}d\xi = \ln\left(\frac{x - \alpha}{x_0 - \alpha}\right)$$

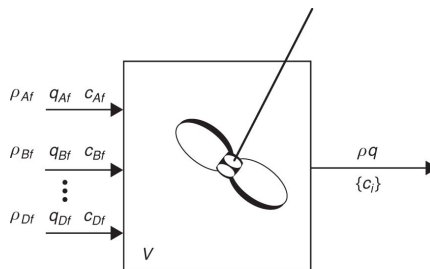$$\int_{x_0}^{x} \frac{1}{\xi}d\xi = \ln\left(\frac{x}{x_0}\right)$$

$$A + \beta B \longrightarrow \mu M$$

$$V\frac{dC_A}{dt} = q_{Af}C_{Af} - qC_A - rV$$

$$V\frac{dC_B}{dt} = q_{Bf}C_{Bf} - qC_B - \beta rV$$

$$V\frac{dC_M}{dt} = \qquad - qC_M + \mu rV$$

$$r = K, \; r = k\,C_A, \; r = k\,C_A\,C_B, \; r = \frac{k\,C_A\,C_B}{1 + k_1\,C_A + k_2\,C_B}$$

$$k = A\,Exp(-E_a/RT)$$

$$V_R\frac{dc_R}{dt} = R\left(c_{Rf} - c_R\right) - \Pi A\left(c_R - c_P\right)$$

$$V_P\frac{dc_P}{dt} = P\left(c_{Pf} - c_P\right) + \Pi A\left(c_R - c_P\right)$$

$$\left(c_{Rf} - c_R\right) = \frac{1}{\left[1 + \dfrac{R}{P} + \dfrac{R}{\Pi A}\right]}\left(c_{Rf} - c_{Pf}\right)$$

UNITS

Mass
1 kg = 1000 g = 0.001 metric ton = 2.20462 lb_m
1 lb_m = 16 oz = 5E-4 ton = 453.59 g = 0.45359 kg

Length
1 m = 100 cm = 1000 mm = 1E6 μm = 1E9 nm = 39.370 in = 3.2808 ft = 1.0936 yd
1 ft = 12 in = 0.30480 m = 30.480 cm
1 in = 2.5400 cm

Volume
1 m^3 = 1000 L = 1E6 cm^3 = 1E6 ml = 35.315 ft^3 = 264.17 gal
1 ft^3 = 1728.0 in^3 = 7.4805 gal = 0.028317 m^3 = 28.317 L = 28317 ml

Force
1 N = 1 kg-m/s^2 = 1E5 dynes = 1E5 g-cm/s^2 = 0.22481 lb_f
1 lb_f = 32.174 lb_m-ft/s^2 = 4.4482 N

Pressure
1 atm = 1.01325E5 N/m^2(Pa) = 1.01325 bar = 760 $mm_{Hg\ at\ 0°C}$ = 33.9 $ft_{H2O\ at\ 4°C}$
1 atm = 14.696 psia
1 bar = 0.1 MPa = 0.98692 atm = 14.504 psia = 750.06 $mm_{Hg\ at\ 0°C}$ = 10.197 $m_{H2O\ at\ 4°C}$

Energy
1 J = 1 N-m = 1 MPa-cm^3 = 1 kgm^2/s^2 = 0.23901 cal = 0.73756 ft-lb_f
1 J = 1E7 ergs = 1E7 g-cm^2/s^2
1 kJ = 0.94781 Btu[see note 1] = 2.7778E-4 kW-h = 0.23901 food calorie

Power
1 W = 1 J/s = 0.2390 cal/s[see note 2] = 0.73756 ft-lb_f/s = 3.4121 Btu/h[see note 1]
1 hp = 550 ft-lb_f/s = 0.70726 Btu/s[see note 1] = 0.74570 kW

Gas Constant, R

= 8.31447 J/mole-K = 8.31447 cm^3-MPa/mole-K = 8.31447 m^3-Pa/mole-K
= 8,314.47 cm^3-kPa/mole-K = 83.1447 cm^3-bar/mole-K = 1.9859 Btu/lbmole-R[see note 1]
= 82.057 cm^3-atm/mole-K = 1.9872 cal/mole-K[see note 2] = 10.731 ft^3-psia/lbmole-R

Gravitational Constants at sea level

g = 9.8066 m/s^2 g/g_c = 9.8066 N/kg g_c = 1 (kg-m/s^2)/N
g = 32.174 ft/s^2 g/g_c = 1 lb_f/lb_m g_c = 32.174 (lb_m-ft/s^2)/lb_f

Faraday's Constant

F = 96,485 J/V

IUPAC Standard Conditions of Temperature and Pressure

T = 0°C = 273.15 K; P = 0.1 MPa; V(ideal gas) = 22711 cm^3/mole;
ρ(water) = 0.99984 g/cm^3 = 8.3441 lb_m/gal

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1. The International Steam Table (IT) BTU.
2. The thermochemical calorie.

If you are considering <u>process equipment,</u> (for which this class will always be at steady state) and neglecting kinetic and potential energy

$$0 = \dot{m}\left(\hat{H}_{in} - \hat{H}_{out} \right) + \dot{Q} + \dot{W}_s$$

In any of the previous equations, the "m" could be replaced by "n" and then "per mass" becomes "per mole"

Note also that in this formulation, any heats of reaction will be automatically taken care of (at standard conditions) in the enthalpies of different substances.