Introduction to Reactor Design, 3K4

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Kevin Dunn, kevin.dunn@mcmaster.ca

McMaster University

Note:
- You may bring in any printed materials to the midterm; any textbooks, any papers, *etc*.
- You may use any calculator during the midterm.
- You may answer the questions in any order on all pages of the answer booklet.
- *Time saving tip*: please **use bullet points** to answer, where appropriate, and **never repeat the question** back in your answer.
- Please note, parts of this exam will require you to apply concepts you have learned in your other core courses, such as 2D, 2F and 3E.
- Use the problem solving strategy we discussed in class: Define, Explore, Plan, Do It, Check, Generalize.
- Also, apply the strategy where you work symbolically, and only substitute in values at the end.
- **Total marks**: 60 marks.
- Total time: 2 hours. There are 3 pages on the exam, please ensure your copy is complete.

General comments on the midterm

- Some people did not read the question completely. They launched into the answer and as they got to the end, came back and read the question, and realized they had to redo some of their work. *Ouch!* That was OK for this test, where you had unlimited time, but it won't work well in an exam.

- Which bring me to the next point: `Define, Explore, Plan, Do It, Check, Generalize.` Most of you draw a picture and write your list of knowns (define), but forget your list of unknowns. But almost no one had a `Plan`: if you plan, it implies you have an end-goal in mind, which implies you have read the question completely.

- A `Plan` will also help you lay out your answer in a structured manner. I'm a patient reader, and will try find your grades, but guaranteed your boss one day is not going to have time for unstructured, cluttered work.

- Related to this, please state where you get your equations from. Don't just write it down. If you see `Where from?` in your answer script with some lost grades, you know why. Write down something like: "From the Ergun equation", or "The mol balance equation for a packed reactor is ..."

- Please use the booklet. Some of you completed the last question on 1 or 2 pages. This is so cramped, and I am unable to provide you feedback, because there is no space left on the page. Use as much paper as you need: both sides so you don't have to flip backwards and forwards.

- Many of you like to go from a complicated equation and just give the final calculated result.

Most times the value you calculated was incorrect. Sorry, but you will lose all grades, I cannot provide method marks. If you show your intermediate steps I can at least isolate your error and give partial grades. Again, this ties in with the fact: use the paper – your tuition fees paid for it anyway.

- Please, never use any red ink in your answers.

- And finally, the most important point: nearly every single time there was a calculation error, it was because you did not work in SI base units, or in SI derived units. Some examples:

  - **min** is not the base SI unit for time, it is seconds

  - **g** is not base SI unit for mass, it is kg

  - **kPa** is not the derived unit for pressure, it is Pa

  - **L** (litres) is not SI, it is m^3

It seems minor (and it surprising to raise this issue at this level), but there are many excellent reasons why the SI system dominates in engineering and science. Even in the USA, engineering and science is done in the SI system. But here is why it is important for you as a Chemical Engineer:

  - Many of the correlations we work with, and dimensionless numbers, only are valid when expressed in SI units.

  - If you work in one set of consistent units all the time, then it is easy to remember what are reasonable values. For example, if you deal with velocity in $m.s^{-1}$, then you quickly build up a mental reference of what is slow and what is fast. But if you are working in $ft.hour^{-1}$ in one problem and then $cm.min^{-1}$ in the next, you never build up this important ability. That ability is crucial in the `Check` step: where you verify your answer is reasonable.

Question 1 [10 = 2 + 2 + 2 + 2 + 2]

Provide single word, or single short sentence answers to each of the following (no lengthy explanations, preferably no equations).

1. Give an example of a chemical reaction which has $\delta > 0$, where δ is the scalar value that measures by how much the system expands or contracts. Be sure to also supply the value of δ for your example.

2. Which of the following assumptions are required to derive the plug-flow design equation $V = \int_{F_{A0}}^{F_A} \frac{dF_A}{r_A}$ from the general mol balance [just write the letter numbers down in your answer book]:

   (a) the system operates at steady state

   (b) the rate of reaction must be constant

   (c) the reactor is well-mixed in the axial direction

(d) there must be no pressure drop in the axial direction

(e) the concentration of A in the centre-line of the reactor is the same as at the wall (also implies there is no boundary layer)

(f) the reactor must have the same diameter all the way from start to end to maintain constant volumetric flow

3. A first order reaction, $-r_A = k_A C_A$ is taking place in a batch reactor. If:

   (a) $k_A = 2 \times 10^{-4}$ hour^{-1}, the reaction can be considered to be _____ (rate / equilibrium) limited.

   (b) $k_A = 2 \times 10^{+4}$ hour^{-1}, the reaction can be considered to be _____ (rate / equilibrium) limited.

4. In general, a liquid-phase CSTR operated at higher flow rates in and out will have a _____ (lower / higher) conversion of the reagent, and will have a _____ (longer / shorter) residence time of material in the reactor.

5. If 3 CSTRs are placed in series, and a second order reaction takes place, with the requirement that each CSTR has the same amount of incremental conversion (e.g. 20% conversion per reactor), then the **last reactor** will be _____ (larger / smaller) in volume than the first reactor, and will have a _____ (greater / smaller) reaction rate than the first reactor.

Solution

1. Air bag reaction: $2\text{NaN}_3 \longrightarrow 2\text{Na} + 3\text{N}_2$ which has $\delta = 1.5$

2. Only options (a) and (e) must hold for the PFR derivation.

3. The (a) smaller rate constant implies the system is rate limited, while the larger constant implies we are limited by equilibrium in terms of our final concentrations.

4. A liquid-phase CSTR operated at higher flow rates in and out will have a *lower* conversion of the reagent, and will have a *shorter* residence time of material in the reactor.

5. If 3 CSTRs are placed in series, and a second order reaction takes place, with the requirement that each CSTR has the same amount of incremental conversion (e.g. 20% conversion per reactor), then the **last reactor** will be *larger* in volume than the first reactor, and will have a *smaller* reaction rate than the first reactor.

Question 2 [5]

The general mol balance (In - Out + Generation = Accumulation) over a boundary can be written symbolically as:

$$F_{j0} - F_j + \int^V r_j dV = \frac{dN_j}{dt}$$

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Start from this *differential* equation and end up showing that the performance equation for a CSTR is the *algebraic* equation:

$$V = \frac{F_{j0} - F_j}{-r_j}$$

Of most importance in your answer is to *show exactly how each assumption applies* in the logical progression from the starting equation to this final equation.

Solution

After the differential equation, we assume the CSTR is operating at steady-state (i.e. all properties remain constant over time), so $\frac{dN_j}{dt} = 0$.

$$F_{j0} - F_j + \int^V r_j dV = 0$$

Then assuming the CSTR is well-mixed, so all properties in the reactor are uniform, which also implies the concentration and other properties leaving are the same:

$$\int^V r_j dV = r_j \int^V dV = r_j V$$

Leading finally to:

$$V = \frac{F_{j0} - F_j}{-r_j}$$

Question 3 [3]

Describe why the constants in a rate expression, for example, the k_A and α constants in the expression $-r_A = k_A C_A^\alpha$, can be most conveniently evaluated in a batch reactor. *Use bullet points!* (no need to show how to calculate k_A and α).

Solution

- Batch reactors *do not* operate at non-steady state
- so the concentrations in the reactor are always changing
- Since these constants are found by evaluating the slope and intercept in a concentration *vs* time plot,
- a batch reactor will provide all the data we require in a single experiment.
- Furthermore, batch reactors are easily controlled (e.g. for isothermal, isobaric operation).

Question 4 [12]

For the liquid phase reaction $A \longrightarrow D$, with second-order kinetics and $C_{A0} = 1 \, \text{mol.L}^{-1}$, we get 35% conversion after 1 hour in a batch reactor. What is the conversion and concentration of A after 1 hour if our raw material has a concentration of $5 \, \text{mol.L}^{-1}$ instead? Explain why your answer makes sense.

Solution

Using the performance equation for a batch reactor, derived from the general mol balance (assuming a well-mixed reactor; does **not assume** steady-state, since batches are by definition not at steady state):

$$t = N_{A0} \int_{X=0}^{X=X} \frac{dX}{-r_A V}$$

Since we have constant volume in the reactor, we can write the molar equation for a batch system dividing by volume:

$$N_A = dN_{A0}(1 - X)$$
$$\frac{N_A}{V} = \frac{N_{A0}(1 - X)}{V}$$
$$C_A = C_{A0}(1 - X)$$

Then using the rate expression $-r_A = k_A C_A^2$ (given that this is second-order kinetics), then substitute into the integral equation:

$$t = \frac{N_{A0}}{V} \int_{X=0}^{X=X} \frac{dX}{k_A C_A^2}$$
$$t = C_{A0} \int_{X=0}^{X=X} \frac{dX}{k_A C_{A0}^2 (1 - X)^2}$$
$$t = \frac{1}{k_A C_{A0}} \int_{X=0}^{X=X} \frac{dX}{(1 - X)^2}$$
$$t = \frac{1}{k_A C_{A0}} \left(\frac{1}{(1 - X)} - 1 \right)$$

Substituting in known values to solve for the rate constant, $k_A = 0.538 \, \text{L.mol}^{-1}.\text{hour}^{-1}$. Then if wish to find the concentration with $C_{A0} = 5 \, \text{mol.L}^{-1}$ (e.g. we change to a different raw material supplier):

$$(1 \, \text{hour}) = \frac{1}{\left(0.538 \, \text{L.mol}^{-1}.\text{hour}^{-1} \right) \left(5 \, \text{mol.L}^{-1} \right)} \left(\frac{1}{(1 - X)} - 1 \right)$$
$$X = 0.73$$

from which we obtain $C_A = C_{A0}(1 - X) = 5(1 - 0.73) = 1.35 \, \text{mol.L}^{-1}$

The higher degree of conversion makes sense because we are starting with a more concentrated raw material (the reaction rate is proportional to the concentration squared).

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Note however, the final concentration achieved with the stronger starting material is $1.35\,\mathrm{mol.L^{-1}}$, but with the weaker reagent it is $C_{A0}(1-X) = 1(1-0.35) = 0.65\,\mathrm{mol.L^{-1}}$, despite the lower conversion. There will be this trade off: the only way to obtain both a high conversion and a low final concentration is to run the batch for longer times.

Question 5 [8]

At 600 K the gas-phase reaction

$$\mathrm{C_2H_4 + Br_2} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{C_2H_4Br_2}$$
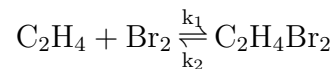
follows elementary kinetics with rate constants $k_1 = 500\,\mathrm{L.mol^{-1}.hour^{-1}}$ and $k_2 = 0.032\,\mathrm{hour^{-1}}$.

Determine an equation whose solution would yield the equilibrium conversion in a constant volume batch reactor. **Note**, the equation should contain conversion as an unknown variable. Equimolar amounts of $\mathrm{C_2H_4}$ and $\mathrm{Br_2}$ may be assumed to be present initially. Use appropriate symbols for any quantities that cannot be determined from the given information; numerical values for all other quantities should be inserted.

Solution

By definition, the equilibrium constant is:

$$K_C = \frac{k_1}{k_{-1}} = \frac{500\,\mathrm{L.mol^{-1}.hour^{-1}}}{0.032\,\mathrm{hour^{-1}}} = \frac{\{\mathrm{C}\}}{\{\mathrm{A}\}\{\mathrm{B}\}}$$

if we define $\{\mathrm{C}\}$ to be the equilibrium concentration of $\mathrm{C_2H_4Br_2}$ and A and B are $\mathrm{C_2H_4}$ and $\mathrm{Br_2}$ respectively.

Since this is a gas-phase system we can use the batch reactor equations, taking expansion/contraction into account and write:

$$C_A = C_{A0}(1 - X)$$
$$C_B = C_{A0}(1 - X)$$
$$C_C = C_{A0}(0 + X), \text{ since there are initially no moles of C present}$$

Define X_{eq} to be the equilibrium conversion, and note that $C_{A0} = \dfrac{y_{A0}P_0}{RT_0}$. But since P_0 is not given we can only work symbolically either in terms of C_{A0} or in terms of P_0. Note that $y_{A0} = 0.5$ and $T = 600\,\mathrm{K}$ are given values.

$$K_C = 15625\,\mathrm{L.mol^{-1}} = \frac{C_{A0}X_{\mathrm{eq}}}{C_{A0}^2(1 - X_{\mathrm{eq}})^2} = \frac{X_{\mathrm{eq}}}{C_{A0}(1 - X_{\mathrm{eq}})^2}$$

Once C_{A0} or P_0 are specified we could solve for X_{eq}.

Question 6 [22]

The following gas phase reaction takes place in a packed-bed reactor under isothermal conditions:

$$2A \longrightarrow B + 3C$$
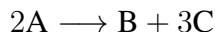
where $-r'_A = kC_A^2$ and $k = 0.6\,\text{L}^2.\text{mol}^{-1}.\text{min}^{-1}.(\text{g catalyst})^{-1}$. The reactor operates at a temperature of 400K. The reactor is fed with an equimolar amount of A and an inert gas, I, at an inlet volumetric flow rate of $q_0 = 10\,\text{L.minute}^{-1}$. The inlet pressure is 200 kPa, and the gas density at these inlet conditions is $7\,\text{kg.m}^{-3}$, with viscosity of $3 \times 10^{-5}\,\text{Pa.s}$.

Additional information that is already known to you is that the reaction will be in a pipe of inside diameter of 5cm and length of 120 m. The catalyst can be packed leaving a void fraction of $\phi = 0.5$; the catalyst pellets are supplied as spheres with diameter of 0.5 cm (the volume of a sphere is $\frac{4}{3}\pi r^3$); and the density of the catalyst is $2000\,\dfrac{\text{kg}}{\text{m}^3 \text{ of pellet}}$.

Show all steps necessary that result in the set of 2 differential equations that can be solved, using computer software. The equations must be specified as the right hand side of:

$$\frac{dX}{dW} = \dots$$
$$\frac{dy}{dW} = \dots$$
$$X(W = 0) = \dots$$
$$y(W = 0) = \dots$$

The equations should be integrated from zero to W = _____ kg

where X is the conversion of species A, $y = \dfrac{P}{P_0}$ and the catalyst weight is W.

All constants in your expressions should be evaluated and given *numerically*. Only the variables X, y and W should remain in your ODEs.

Solution

Follow the problem solving strategy learned in class: `Define, Explore, Plan, Do It, Check, Generalize`. Numbers is square brackets represent where the grades were allocated. Negative grading was using in most people's scripts, i.e. you start with 22 grades and I only subtract where there are errors. For example, a grade of **[1]** requires the value *and* the units to be correct.

`Define`: write down what we know and what we don't know, and also draw a picture. For example, here's my picture on my copy of the test:
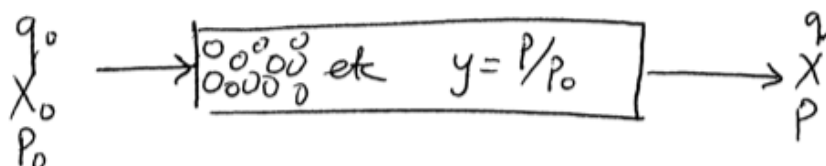
Known:

- Isothermal: implies $T_0 = T = 400\,\text{K}$ **[1]**

- $2\text{A} \longrightarrow \text{B} + 3\text{C}$ can be written as $\text{A} \longrightarrow \frac{1}{2}\text{B} + \frac{3}{2}\text{C}$

- where $-r'_A = kC_A^2$

- $k = 0.6\,\text{L}^2.\text{mol}^{-1}.\text{min}^{-1}.(\text{g catalyst})^{-1} = 1 \times 10^{-5}\,\text{m}^6.\text{mol}^{-1}.\text{s}^{-1}.(\text{kg catalyst})^{-1}$ **[1]**

- Equimolar feed of A and an inert; this implies $y_{A0} = 0.5$ and $y_{I0} = 0.5$ **[1]**

- $q_0 = 10\,\text{L.minute}^{-1} = 0.00016667\,\text{m}^3.\text{s}^{-1}$ **[1]**

- $P_0 = 200\,\text{kPa}$

- $\rho_0 = 7\,\text{kg.m}^{-3}$

- $\mu = 3 \times 10^{-5}\,\text{Pa.s}$

- Inside diameter = 5cm, so cross-sectional area = $A_C = \pi(2.5 \times 10^{-2}) = 0.00196\,\text{m}^2$ **[1]**

- Pipe length = $120\,\text{m}$

- Reactor volume = $(0.00196\,\text{m}^2)(120\,\text{m}) = 0.2356\,\text{m}^3$

- $\phi = 0.5$

- $D_p = 0.5\,\text{cm} = 0.005\,\text{m}$

- $\rho_C = 2000\,\dfrac{\text{kg}}{\text{m}^3\text{ of pellet}} = 2000\,\dfrac{\text{kg}}{\text{m}^3\text{ of solids in the reactor}}$ **[1]**

Unknown:

- W, the catalyst weight

- P, the pressure profile along the reactor

- X, the conversion profile along the reactor

- δ

- ε

- β_0 from the Ergun equation

- α from the Ergun equation

- F_{A0}

Explore:

- Gas phase reaction: expansion and contraction is going to be important: we will need a δ and ε. Se we can go back to our `Define` step and add those as two unknowns

- Packed-bed reactor: there's going to be pressure drop. This means we will have to use the Ergun equation, with unknowns β_0 and α. Let's go add those to our list of unknowns above.

- Do we need a basis? Yes: we are working in terms of the catalyst weight profile along the length of the reactor. Our other basis is that species A is the limiting reactant.

- What is our boundary? The inside of the PBR.

Plan (*note in an exam you don't have to write this part down, but have a mental plan; I've written it here so you can see the thought process I used when solving this problem*). I follow the numbers in the flow chart plan that was handed out in class on 04 February.

1. General mole balance: OK

2. Use the PBR equation, but there is an unknown, F_{A0}, let's add it to our list on knowns above.

3. The reaction rate is given, but not in terms of conversion.

4. We are given the reaction rate though in terms of concentration.

5. We can get concentrations in terms of conversion though from the flow table.

6. Does not apply: we do not have $P = P_0$

7. This is the Ergun equation, and it is in the format we need for this problem. We have already written down those unknowns.

8. This is exactly what the problem requires us to do: set up the ODEs to solve later with a computer.

We are ready to start the problem now to solve the aim: get the ODE's and the initial conditions.

Do It

We will work only in SI units below, so I won't show all the units in all equations below.

1. Mole balance: OK

2. Select the PBR equation, that's the system we are dealing with: $F_{A0}\dfrac{dX}{dW} = -r'_A$ **[1]**

3. The reaction rate is given

4. $-r_A = kC_A^2$

5. Let's use the stoichiometric table to get conversions:

   - $\delta = \dfrac{1}{2} + \dfrac{3}{2} - 1 = 1$ **[1]**

   - $\varepsilon = y_{A0}\delta = (0.5)(1) = 0.5$ **[1]**

   - $C_A = C_{A0}\left(\dfrac{1-X}{1+\varepsilon X}\right)\left(\dfrac{P}{P_0}\right)$ **[1]**

   - No need to write the other species in terms of X, we only need $C_A = f(X)$

   - So $-r'_A = kC_A^2 = 1 \times 10^{-5}C_{A0}^2\dfrac{(1-X)^2}{(1+\varepsilon X)^2}\left(\dfrac{P}{P_0}\right)^2$ **[1]**

   - Simplify a bit: $-r'_A = 1 \times 10^{-5}C_{A0}^2\dfrac{(1-X)^2}{(1+\varepsilon X)^2}(y)^2$

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- Note that I'm dropping all units, because as long as I work in SI, everything will be OK (but I will check at the end).

- Also note that $F_{A0} = C_{A0}q_0 = \dfrac{y_{A0}P_0}{RT_0} \cdot q_0 = \dfrac{(0.5)(200000)}{(8.314)(400)}(0.00016667) = (30.07)(0.00016667) = 0.005\,\text{mol.s}^{-1}$ **[1]**

6. Does not apply.

7. The Ergun equation applies for a packed bed, with pressure drop:

$$\frac{dy}{dW} = -\frac{\alpha}{2y}(1 + \varepsilon X) \qquad \textbf{[1]}$$

$$\alpha = \frac{2\beta_0}{A_C \rho_C (1 - \phi)P_0}$$

$$\beta_0 = \frac{G(1 - \phi)}{\rho_0 D_p \phi^3}\left[\frac{150(1 - \phi)\mu}{D_p} + 1.75G\right]$$

We know all the terms for β_0 except for G

G = mass flux = mass flow per unit time per unit area

$$G = \frac{\rho_0 q_0}{A_C} = \frac{(7\,\text{kg.m}^{-3})(0.00016667\,\text{m}^3.\text{s}^{-1})}{0.00196\,\text{m}^2} = 0.595\frac{\text{kg}}{\text{s.m}^2} \qquad \textbf{[2]}$$

$$\beta_0 = \frac{0.595(1 - 0.5)}{(7)(0.005)(0.5)^3}\left[\frac{150(1 - 0.5)(3 \times 10^{-5})}{0.005} + 1.75(0.595)\right]$$

$$\beta_0 = 68\,[0.45 + 1.04] = 101.3\,\text{Pa.m}^{-1} \qquad \textbf{[1]}$$

$$\alpha = \frac{2 \times 101.3\,\text{Pa.m}^{-1}}{0.00196\,\text{m}^2(2000\,\text{kg.m}^{-3})(1 - 0.5)(200000\,\text{Pa})} = 5.17 \times 10^{-4}\,\text{kg}^{-1} \qquad \textbf{[1]}$$

8. Finally, bring the two ODE equations together to present the final answer only in terms of X, W and y:

$$\frac{dX}{dW} = \frac{-r'_A}{F_{A0}} = \frac{(1 \times 10^{-5})(30.07)^2\dfrac{(1 - X)^2}{(1 + \varepsilon X)^2}(y)^2}{0.005\,\text{mol.s}^{-1}} = 1.808\frac{(1 - X)^2(y)^2}{(1 + 0.5X)^2} \qquad \textbf{[1]}$$

$$\frac{dy}{dW} = -\frac{\alpha}{2y}(1 + \varepsilon X) = -\frac{5.17 \times 10^{-4}}{2y}(1 + 0.5X) \qquad \textbf{[1]}$$

$$X(W = 0) = 0.0 \qquad \textbf{[1]}$$
$$y(W = 0) = 1.0 \qquad \textbf{[1]}$$

The equations should be integrated from zero to $W = 235.6\ \text{kg}$ **[1]**

We can calculate how much catalyst there is from:

$$W = (1 - \phi)(V)\rho_C = (1 - 0.5)(0.2356\,\text{m}^3)\left(2000\,\frac{\text{kg}}{\text{m}^3\text{ of solids in the reactor}}\right) = 235.6\,\text{kg}.$$

- The catalyst weight of 235.6 kg (a quarter metric ton) seems reasonable for a reactor of 120 m in length and 5cm in diameter. Several students calculated a value of 0.00013 grams of catalyst, due to using an the pellet volume, instead of the reactor volume. Recognize that this little catalyst is not a reasonable value for a reactor of 120 m long. Other students recorded values in the millions of tons.

- δ and ε are positive, which we expect for a reaction where there is expansion.

- The value for G seems reasonable: gases are very light, so 0.6 kg of gas flowing past a point every second seems like a lot.

- Values for α and β_0 are hard to judge, because we have no familiarity with typical values yet. But in a real-life situation we would integrate the ODEs (you will do that in a future assignment), and check that the pressure drop given by the above equation is reasonable.

- The signs in the ODE's appear correct:

  1. $\dfrac{dX}{dW} = 1.808\dfrac{(1-X)^2(y)^2}{(1+0.5X)^2} > 0$ for all values of $0 \leq X \leq 1.0$ and $0 \leq y \leq 1.0$

  2. $\dfrac{dy}{dW} = -\dfrac{5.17 \times 10^{-4}}{2y}(1+0.5X) < 0$ for all values of $0 \leq X \leq 1.0$ and $0 \leq y \leq 1.0$

  The first shows the conversion X will increase as we proceed down the length of the reactor. The second shows that y will decrease along the length of the reactor.

Generalize

Generalization is a form of reflecting/thinking about what you learned, and *how* you efficiently/inefficiently solved the problem and can do it better/faster/more accurately next time:

1. We have started to get an idea of α, β_0 and G order-of-magnitude values for gas-phase systems.

2. Values that are calculated and used in more than one equation, such as A_C = pi r^2 and $G = \dfrac{\rho_0 q_0}{A_C}$, should be calculated and subbed in symbolically. Several people put the values in, and calculated it correctly in one equation, then recalculated it incorrectly in another.

3. The key to solving this problem correctly, and any other problem where we are dealing with many variables, is to work in a consistent set of units. Many students mixed units: e.g. using minutes, litres and kPa, instead of using pure SI units. Companies and their suppliers often work in different units; always work, where possible in SI units – there are many reasons why it is the international standard.

The end.