Adiabatic Calorimetry of a Thermal Runaway Reaction

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COMSOL Conference October 3, 2019

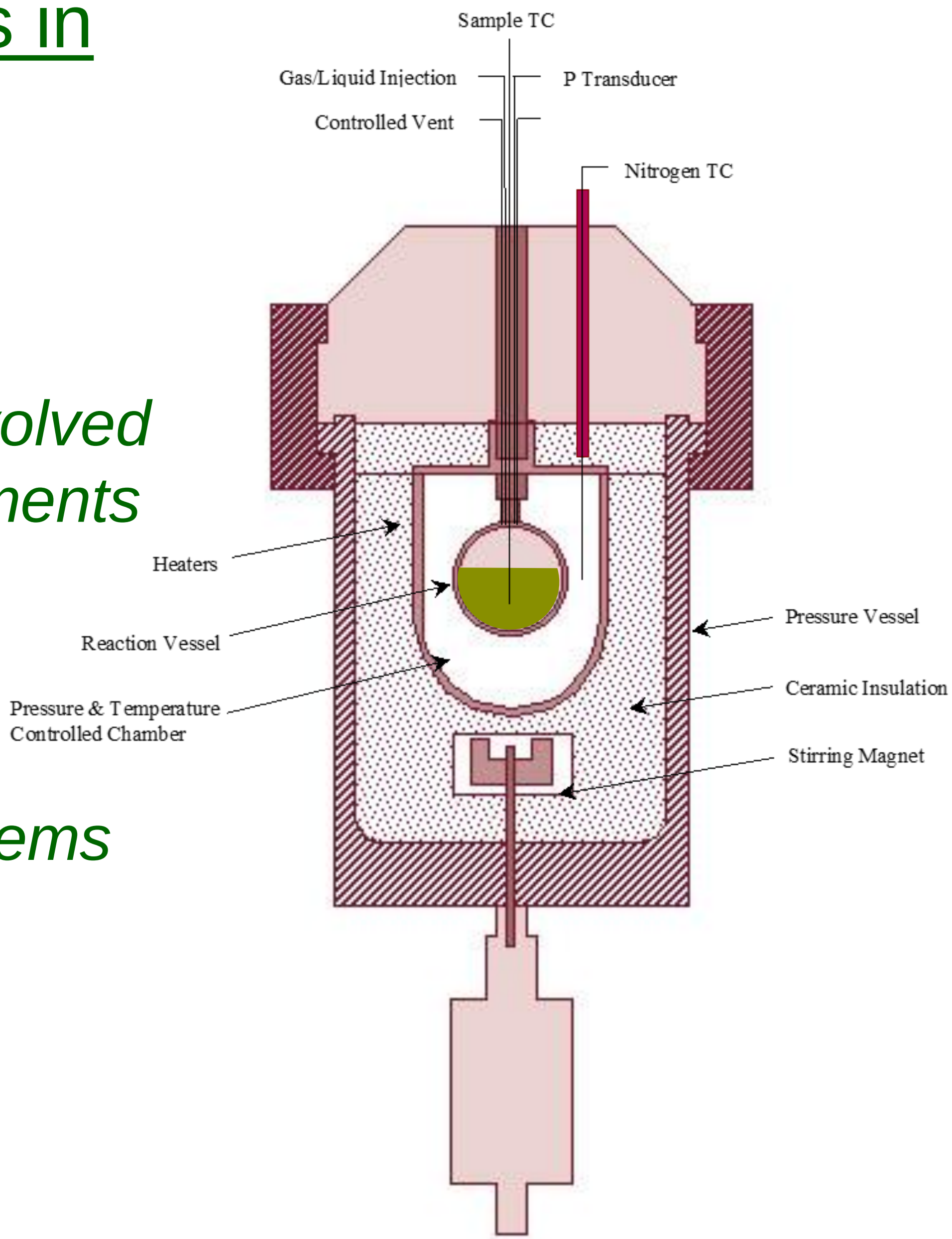
Background

Testing energetic materials in the *APTAC*

(Automatic Pressure Tracking Adiabatic Calorimeter)

Accounting for the total heat evolved in adiabatic calorimeter experiments typically assumes that the cell absorbs heat from the sample uniformly across the cell.

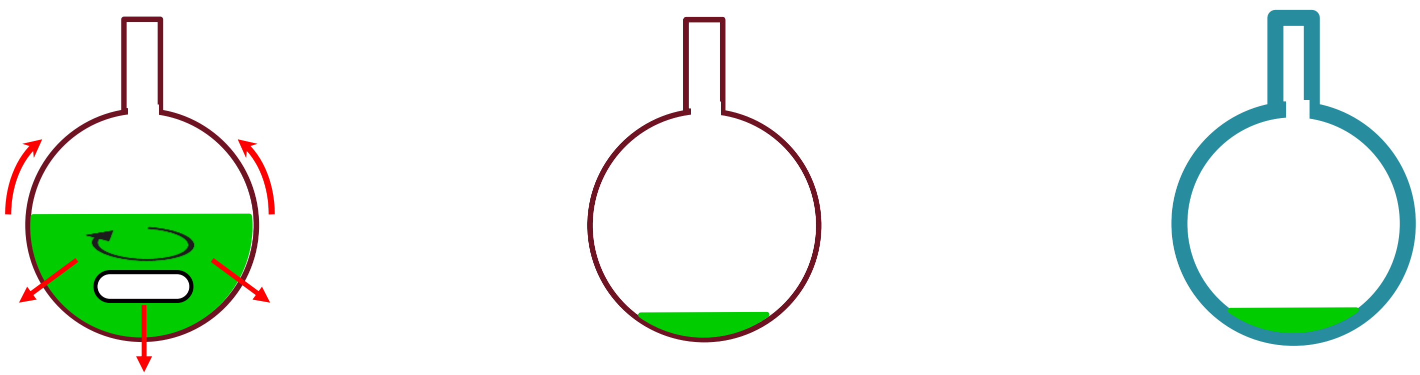
In some circumstances, this seems to be unrealistic



Background (cont'd)

Consider testing of an explosive material, such as di-tert-butyl peroxide (DTBP), in the APTAC.

Charging too much material in an APTAC cell could damage the calorimeter so testing is sometimes performed with only *2-3* ml (1½ to 2½ g) of material in a standard *glass* test cell.



Typical configuration   Small charge   Small charge/Glass cell

Heat Conduction in Cell Wall

Thermal conductivity (Engineering ToolBox, etc.)

$k_{titanium}$ ≈ 22 W/m-K (15 – 25 W/m-K)

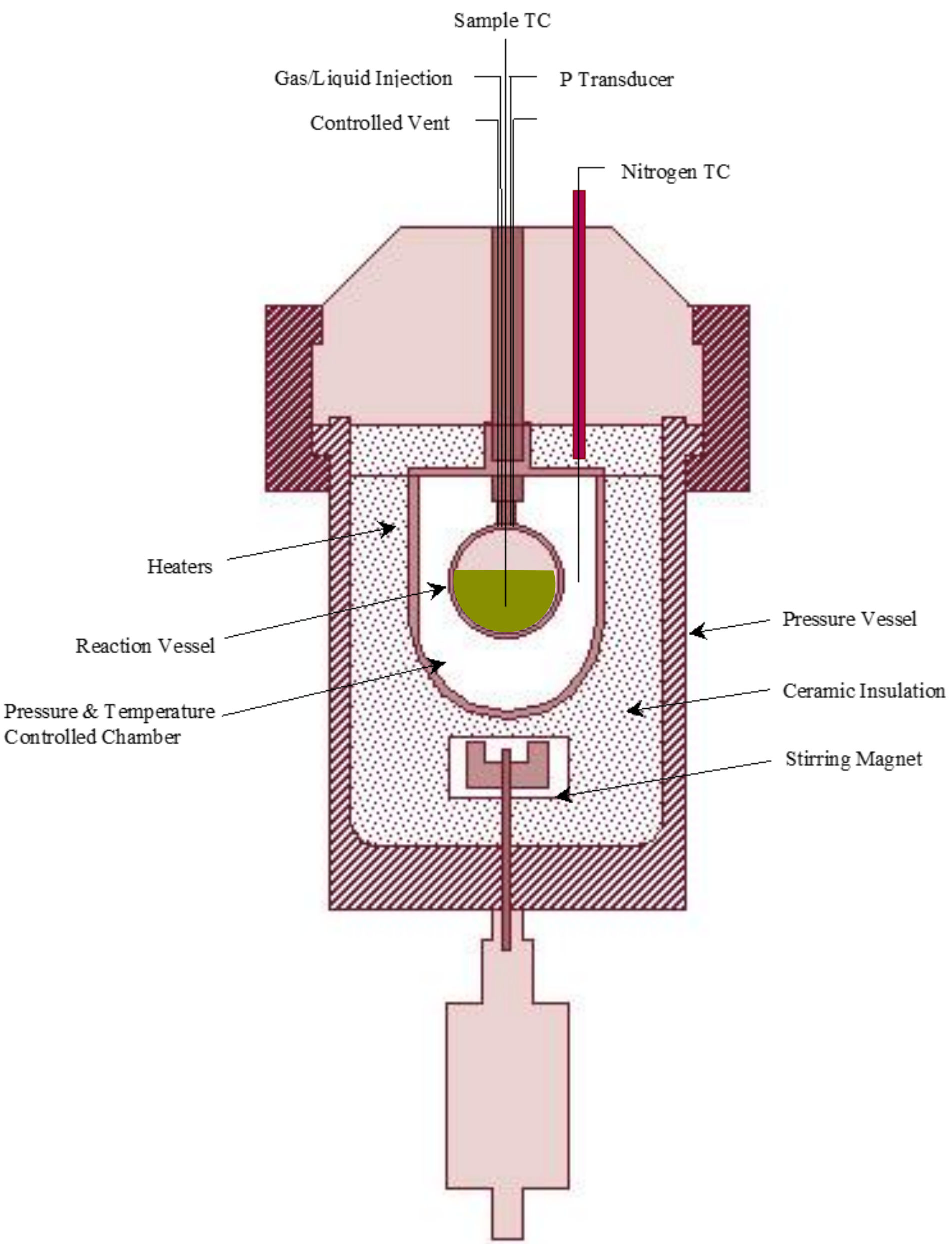
k_{glass} ≈ 1 W/m-K (0.8 – 1.2 W/m-K)

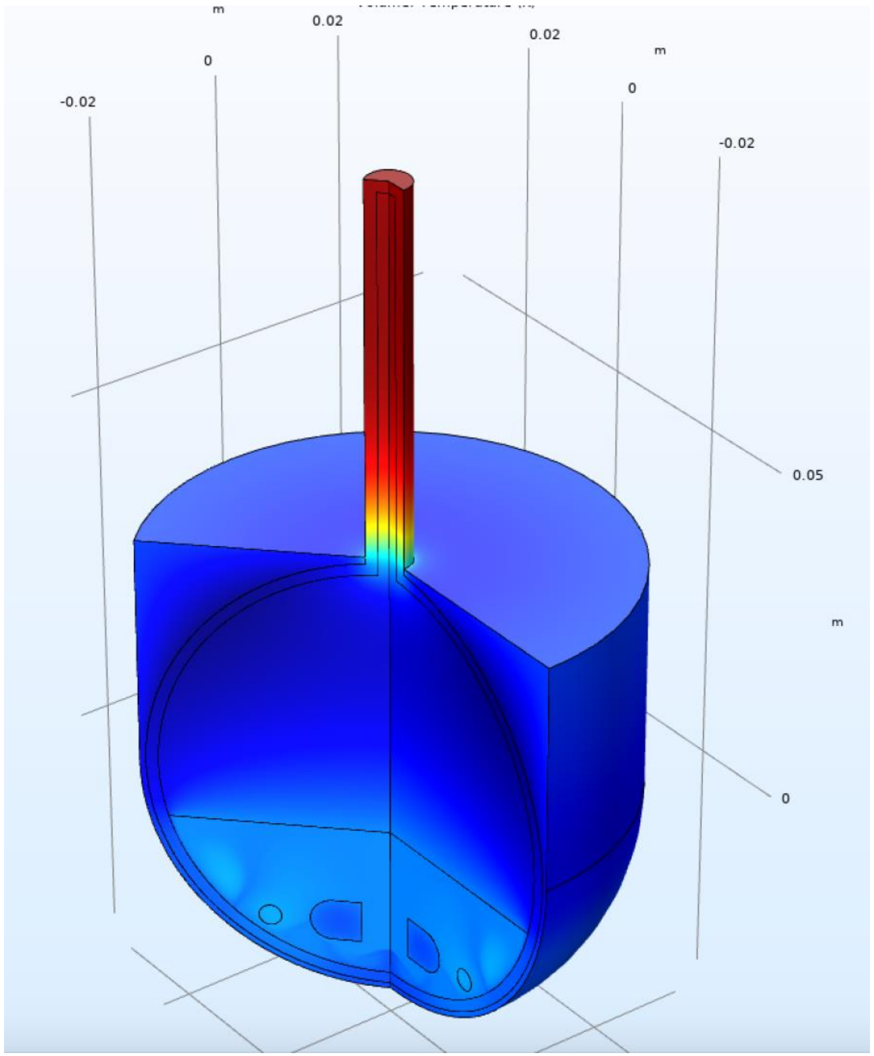
Approach

To understand the behavior in an APTAC cell, a COMSOL Multiphysics® model was developed in 2D-Axisymmetric geometry:

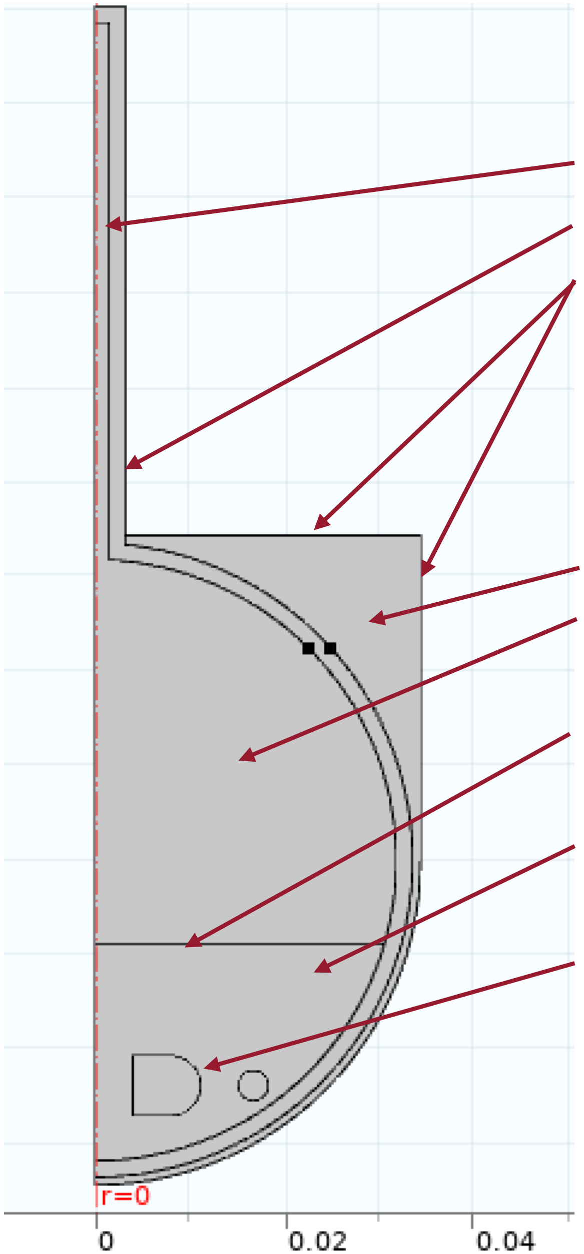
- Heat transfer including radiation
- Exothermic reaction (DTBP as a test case)
- Fluid flow including natural convection
- Transient behavior

Model


Sample TC
Gas/Liquid Injection
P Transducer
Controlled Vent
Nitrogen TC
Heaters
Reaction Vessel
Pressure & Temperature
Controlled Chamber
Pressure Vessel
Ceramic Insulation
Stirring Magnet


m
0.02
0.02
0
m
0
-0.02
-0.02
0.05
m
0

GEOM + Model



Neck: 6 cm

Glass: 1.73 mm thick; 6.7 cm Diameter

Guard Heaters

Buffer Gas: Nitrogen (Laminar w Natural Conv)

Vapor Phase: Nitrogen (Turbulent k-ε)

Vapor-Liquid Interface (Continuity)

Liquid Phase: Toluene+DTBP (Turbulent k-ε)

Spinbar: Donut (Elliptical)

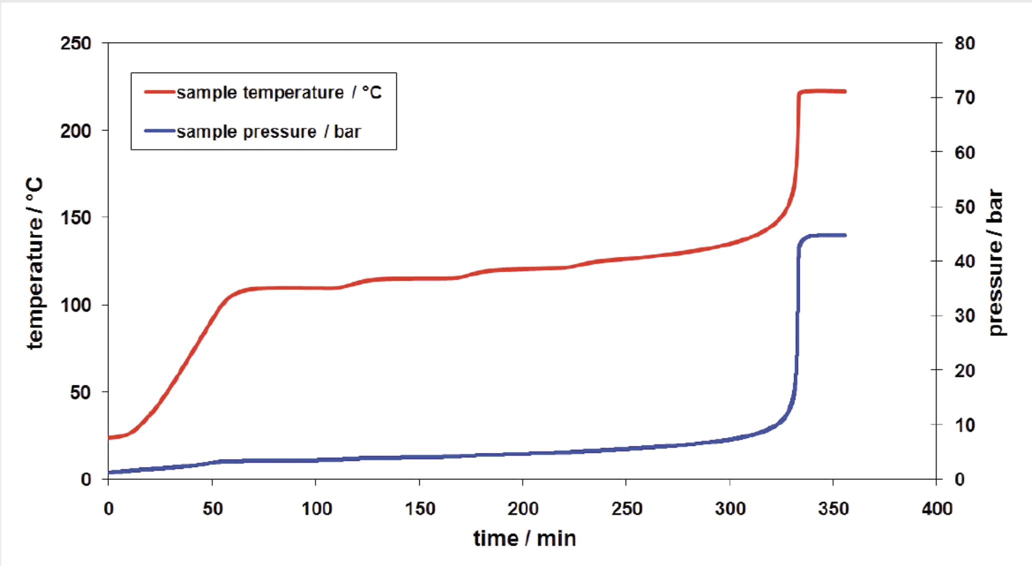
Assumptions

Assumptions include:

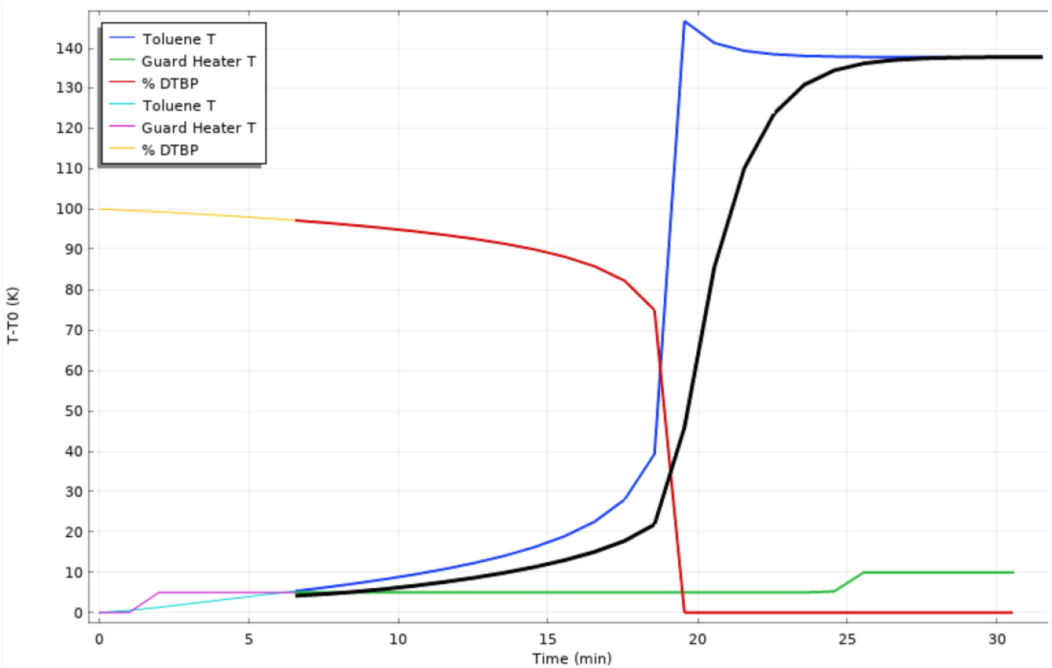
1. Thick glass (3 mm) or thin titanium (0.5 mm) cell
2. 2D axisymmetric geometry
3. Various volumes of reactive solution (25 wt% DTBP in toluene)
4. Wall heaters match sample TC temperature
5. Turbulent flow, k-ε model, in liquid and vapor
6. Symmetrical, donut-shaped magnetic stirrer @ 500 RPM
7. Nitrogen vapor phase; pressurized nitrogen bath
8. Simple, 1st-order, T-dependent kinetics, with ΔH_{rxr}
9. Radiant heat transfer from heaters across nitrogen bath
10. Ignore thermal expansion of liquid

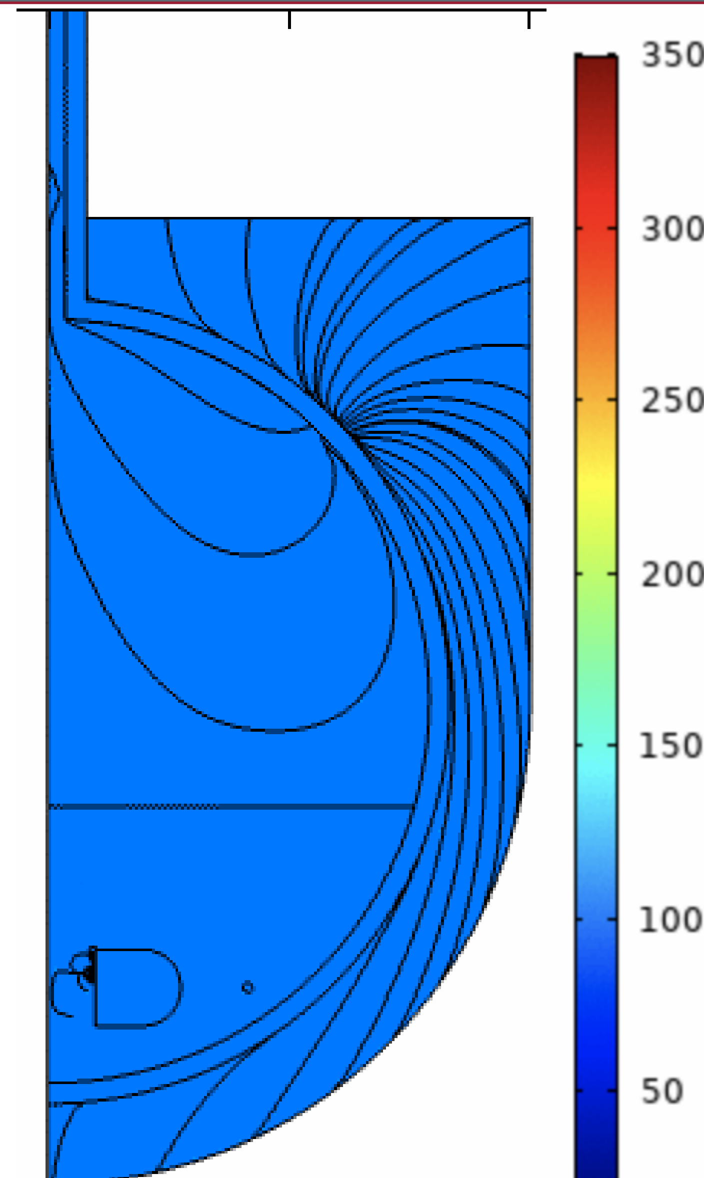
11. Ignore evaporation/condensation of toluene or DTBP
12. Ignore liquid-vapor equilibrium
13. Fixed, flat gas-liquid interface
14. 2D-axisymmetric flow

Data and Simulation



Thermal runaway reaction of a 20% solution of di-tert. butyl peroxide (DTBP) in toluene.





Glass cell
38 cc sol'n

Conclusions

1. “Good” agreement between experiment and simulation

2. Significant spatial variation in 3D model vs 0D model

3. Variation due to thermal inertia of glass reactor

4. Recoil may be due to missing condensation on glass

Future Work

1. Compare with lab results (reactivity, fluid flow)
2. Include condensation on reactor walls
3. Compare high charge & low charge results
4. Convert to a 3D model

Questions?