ChE 344
Reaction Engineering and Design

Lecture 19: Thurs, March 24, 2022

Intro to Unsteady state energy balance and Safety

Video for today: https://www.youtube.com/watch?v=C561PCq5E1g

http://umich.edu/~safeche/courses/ChemicalReactionEngineering.html

Reading for today's Lecture: Chapter 13

Reading for Lecture 20: Chapter 9

Lecture 19: Unsteady state reactor energy balance and Safety
Related Text: Chapter 13

Unsteady state operation is a particularly risky portion of operating chemical reactors. It is important to understand the risks involved with loss of temperature control for exothermic reactions which can cause fatal accidents.

As a note, we won't cover unsteady state PFRs/PBRs as they require more complex solvers since the dependent variables depend both on volume (location in reactor) and time.

For a semi-batch or CSTR with no shaft work and a large coolant flow rate such that the heat exchange fluid temperature is constant

$$\frac{dT}{dt} = \frac{\overbrace{(\Delta H_{rxn})(r_A V)}^{\dot{Q}_{gs}} - \left[\overbrace{F_{A0}\sum \theta_i C_{P,i}(T - T_0) + \big(UA(T - T_a)\big)}^{\dot{Q}_{rs}}\right]}{\sum N_i C_{P,i}}$$

For a batch reactor with no flows in/out and no shaft work, and large coolant flow rate:

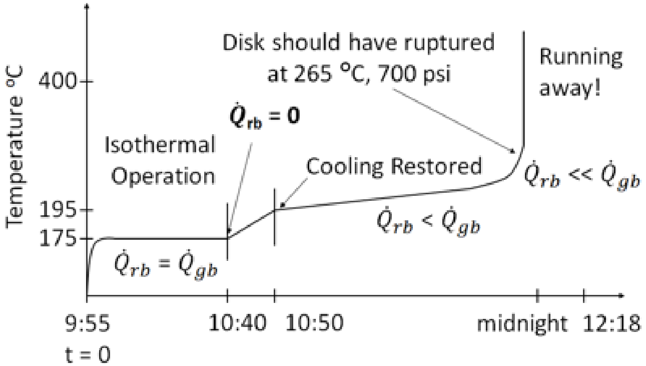
$$\frac{dT}{dt} = \frac{\overbrace{(\Delta H_{rxn})(r_A V)}^{\dot{Q}_{gb}} - \left[\overbrace{\big(UA(T - T_a)\big)}^{\dot{Q}_{rb}}\right]}{\sum N_i C_{P,i}}$$

A change in temperature with time will occur if the generation and removal terms are not equal. For a first order reaction in a batch reactor:

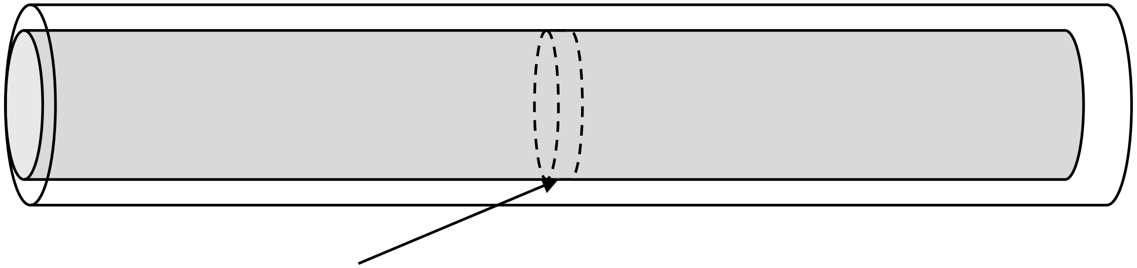
$$\dot{Q}_{gb} = (\Delta H_{rxn})(r_A V) = -kC_A(\Delta H_{rxn} V) = -Ae^{-E_a/RT} C_A(\Delta H_{rxn} V)$$

$$\dot{Q}_{rb} = UA(T - T_a)$$

While both terms will increase with temperature, the generation term will increase exponentially, while the removal term will only increase linearly. This increase with temperature will lead to a larger difference between generation and removal, and will cause the temperature to 'runaway'. Safety Module 1 discusses this, and here is the reactor temperature profile with time.



For PFRs at steady state w/ 1 reaction: (Chapter 12 review)



Considering a small section of the reactor: If more heat is generated in that section (Q_g) than removed (Q_r), fluid will exit that section at higher temperature, but the temperature in that section is constant in time (steady state)

$$\frac{dT}{dV} = \frac{r_A \Delta H_{rxn} - Ua(T - T_a)}{\sum F_i C_{P,i}}$$

$$Q_g = r_A \Delta H_{rxn}$$

$$Q_r = Ua(T - T_a)$$

Total heat in entire reactor is $\int Q_g dV \; and \; \int Q_r dV$

Q_g, Q_r have units of kJ min^{-1} L^{-1}

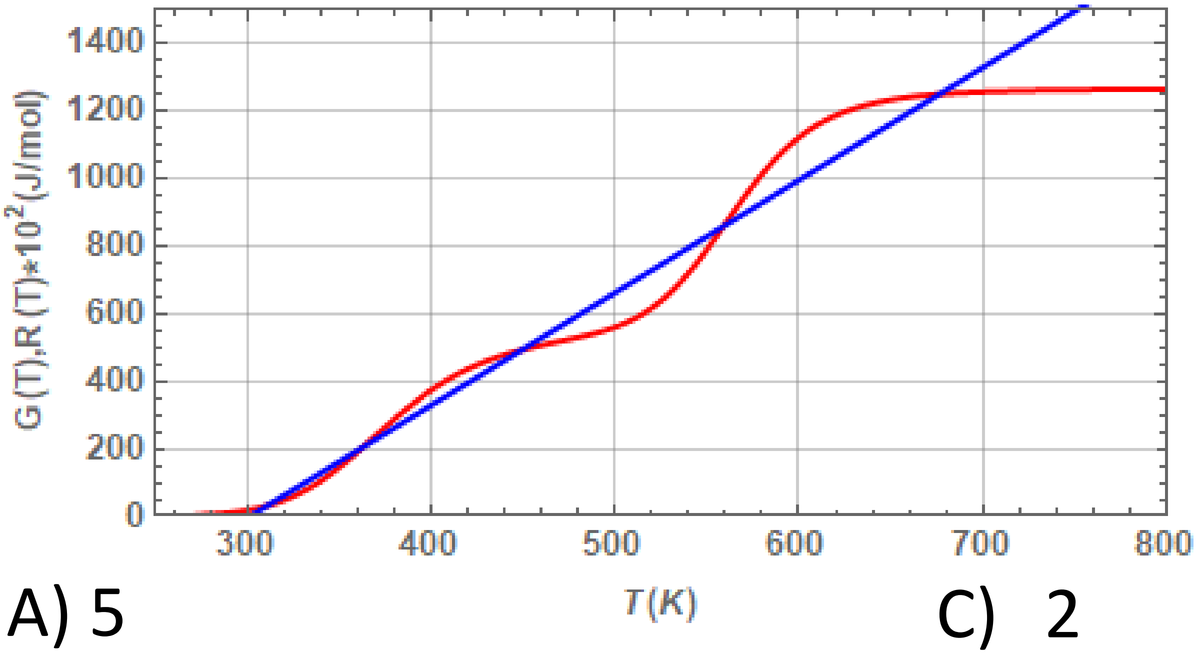
Total heat will have units of kJ min^{-1}

For well-mixed reactors (e.g., CSTRs) at steady state: (Ch. 12)

$$\underbrace{-[\Delta H_{rxn}(T_{ref})]X}_{Reaction\ heat\ generated=G(T)} = \underbrace{C_{P0}(1+\kappa)(T-T_c)}_{\substack{Heat\ removed\ by:\\ coolant\ and\ reactor\ effluent=R(T)}}$$

<u>Discuss with your neighbors</u>:

How many <u>stable</u> steady states are there?



have units of kJ mol^{-1}

A) 5

C) 2

[✓ B) 3]

D) No stable steady states

Energy balance for **un**steady state systems that are well mixed (e.g., batch/semi-batch reactors, CSTRs during startup) with no shaft work, and large coolant flow rate (Chapter **13**)

$$\frac{dT}{dt} = \frac{\overbrace{(\Delta H_{rxn})(r_A V)}^{\dot{Q}_{gb}\ or\ \dot{Q}_{gs}} - \left[\overbrace{F_{A0}\sum \theta_i C_{P,i}\,(T - T_0) + \big(UA(T - T_a)\big)}^{\dot{Q}_{rs}}\right]}{\sum N_i C_{P,i}}$$

$\dot{Q}_{gb}$ will have units of kJ min^{-1}, it is *similar* but **not** Q_g

Meaning for a batch reactor "s" is for semi-batch/CSTR

We will use unsteady state energy balances to understand concepts of safety (T runaway with time $\frac{dT}{dt}$)

Safety:

“Just because nothing bad has happened <u>doesn’t</u> mean you’re operating safely!”

Some examples and case studies :

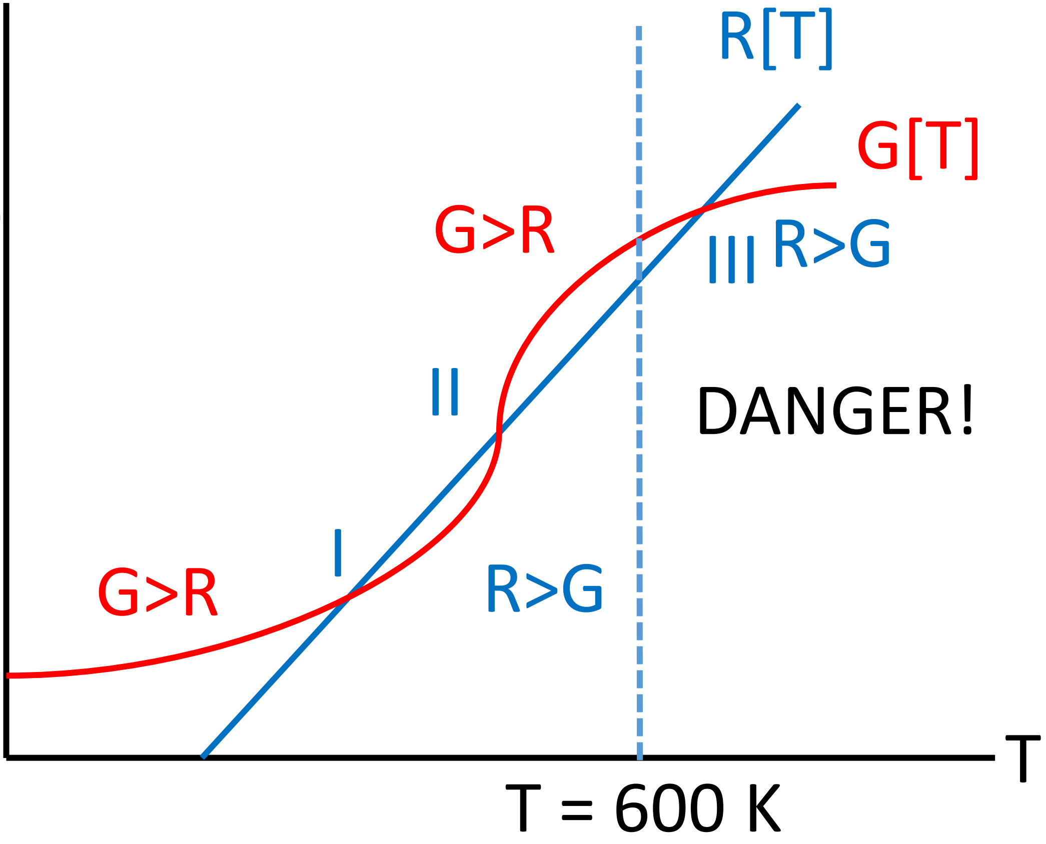
- Multiple steady states for CSTR
- Explosion at T2 Laboratories (MCMT production) Safety Module 1
- Nitroaniline (Monsanto) Safety Module 2a, on Homework 8
- Synthron Runaway Reaction Safety Module 2b, on Homework 8 (click on the title itself to get module)

You should *conceptually* think about these types of problems but we will not do a lot of solving them out (and I won’t expect you to do them out fully)

With your neighbors:

Recall that last week we identified steady state points I and III are stable, II is unstable.

R[T] (removed)
or G[T] (generated)



If our reactor melts at 600 K, which are temperatures to operate at safely?

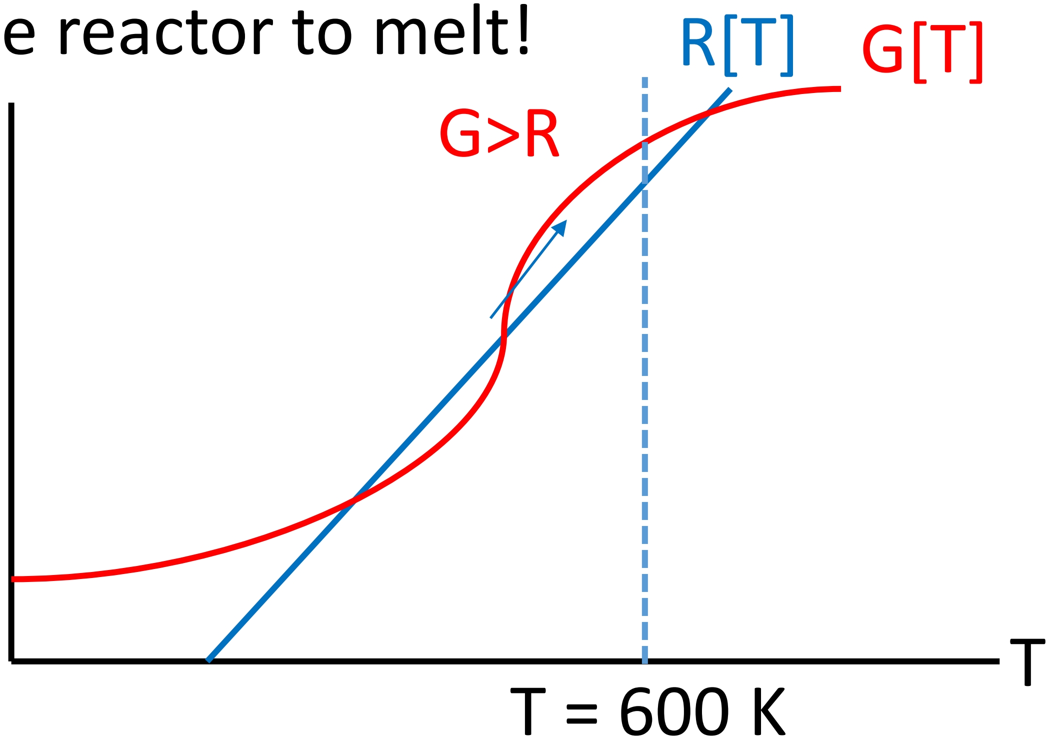
A) I and II are safe

B) I and III are safe

C) All are safe

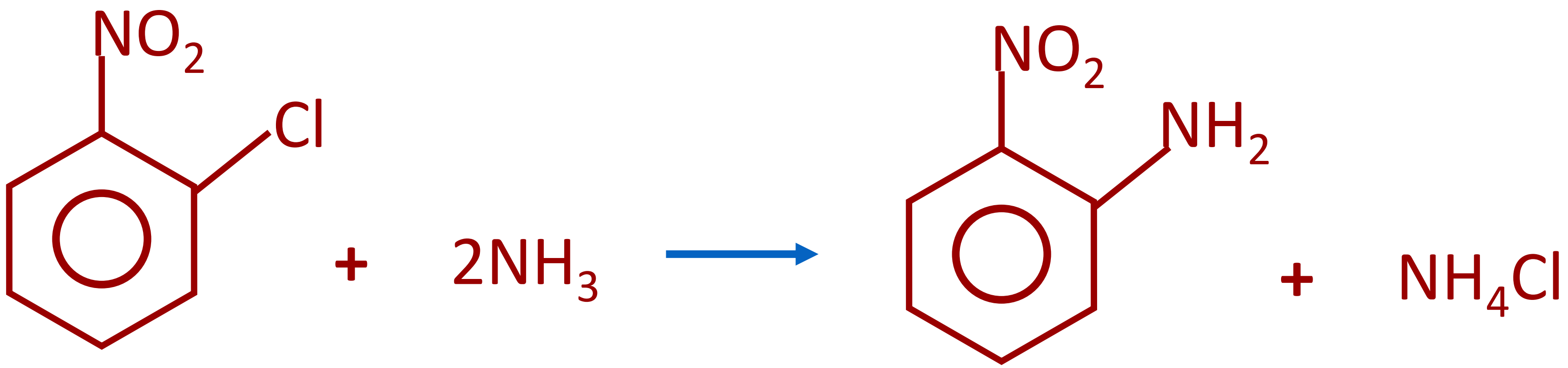
[✓ D) Only I is safe]

Although point II is below the minimum melting temperature of the reactor, it is an unstable point. So if there is a slight perturbation to the reactor such that the temperature gets higher, the generation term being larger than removal will cause a further increase in T to a new steady state (III) that will cause the reactor to melt!



For safety, important to not only consider what will happen if everything goes perfectly!

Monsanto:
Nitroaniline from ammonia- Safety Module 2a (HW9)



ONCB + Ammonia → Nitroanaline + Ammonium Chloride

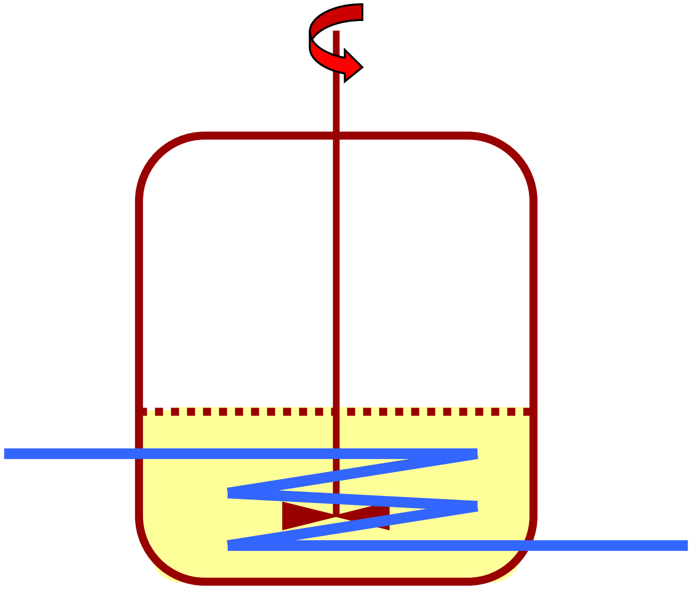
orthonitrochlorobenzene

Precursor in pharma

Batch reactor operation

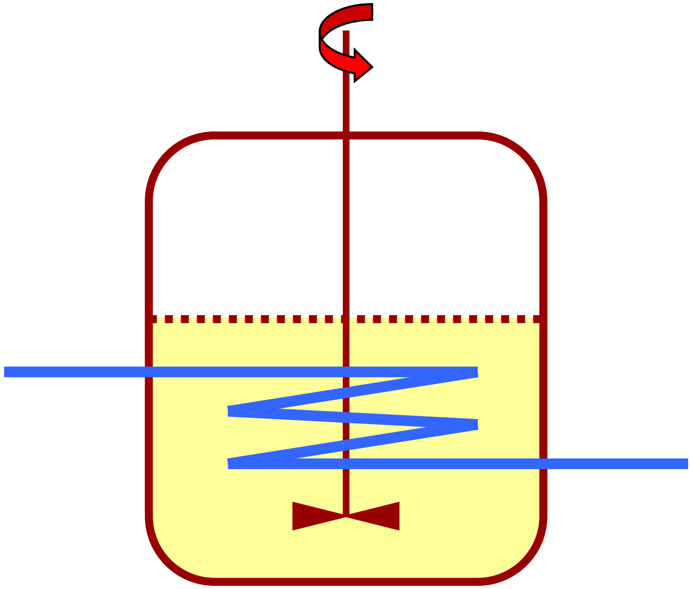
Management said: Triple the production!

Management said, “there is extra space in the reactor, why not use it to make triple the product?”



Old

3 kmol ONCB
43 kmol Ammonia
100 kmol Water
V = 3.25 m^3



New

9 kmol ONCB
33 kmol Ammonia
100 kmol Water
V = 5 m^3

The batch reactor had been started, with heat generated by the reaction, and removed by the heat exchanger (via the heat exchange fluid). No flow in/out

$$\frac{dT}{dt}=\frac{\overbrace{(\Delta H_{rxn})(r_AV)}^{\dot{Q}_{gb}}-\left[\cancel{F_{A0}\sum\theta_iC_{P,i}\,(T-T_0)}+\overbrace{\left(UA(T-T_a)\right)}^{\dot{Q}_{rb}}\right]}{\sum N_iC_{P,i}}$$

To maintain isothermal operation, heat removed equaled the heat generated by the reaction. If coolant flow rate is fast enough, T_a is constant

Generation: $\dot{Q}_{gb}=(\Delta H_{rxn})(r_AV)=-k_1C_AC_BV\Delta H_{rxn}$

Removal:

$$\dot{Q}_{rb}=UA(T-T_a)=35.85kcal\,min^{-1}K^{-1}(T-T_a)$$

After 45 minutes of isothermal operation, the heat exchanger failed, such that there is no longer removal of heat: $\dot{Q}_{rb}$ =0

X = 0.033, T = 448 K at time of heat exchanger failure

Generation of heat remains the same:

$$(\Delta H_{rxn})(r_A V) = 3850\ kcal/min$$

Removal goes to zero, such that the temperature rises (20 degrees in 10 minutes).

So for 10 minutes (t = 45 to 55 min, before the heat exchanger came back on) the reactor was operating adiabatically. Once the heat exchanger comes back on, due to the increase in T, even with a slightly higher X (lower C_A, C_B):

$$(\Delta H_{rxn})(r_A V) = 6591\ kcal/min$$

Discuss with your neighbors:

At 10:50 pm, when the heat exchanger is back on, heat removed is 35.85 $kcal\ min^{-1}K^{-1}(T - T_a)$ and the heat generated is 6591 $kcal/min$ at T = 468 K.
If T_a = 298 K, $\sum N_i C_{P,i}$ = 2490 kcal/K, what will the temperature be at 11:40 pm (50 minutes later)?
Assume $\dot{Q}_{gb}$ and $\dot{Q}_{rb}$ stay the same during those 50 min.*

$$\frac{dT}{dt} = \frac{\dot{Q}_{gb} - \dot{Q}_{rb}}{\sum N_i C_{P,i}}$$

$$= \frac{6591\ kcal/min - 35.85\ kcal\ min^{-1}K^{-1}(468\ K - 298K)}{2490\ kcal/K}$$

$$= 0.2\ K/min$$

A) 468 K

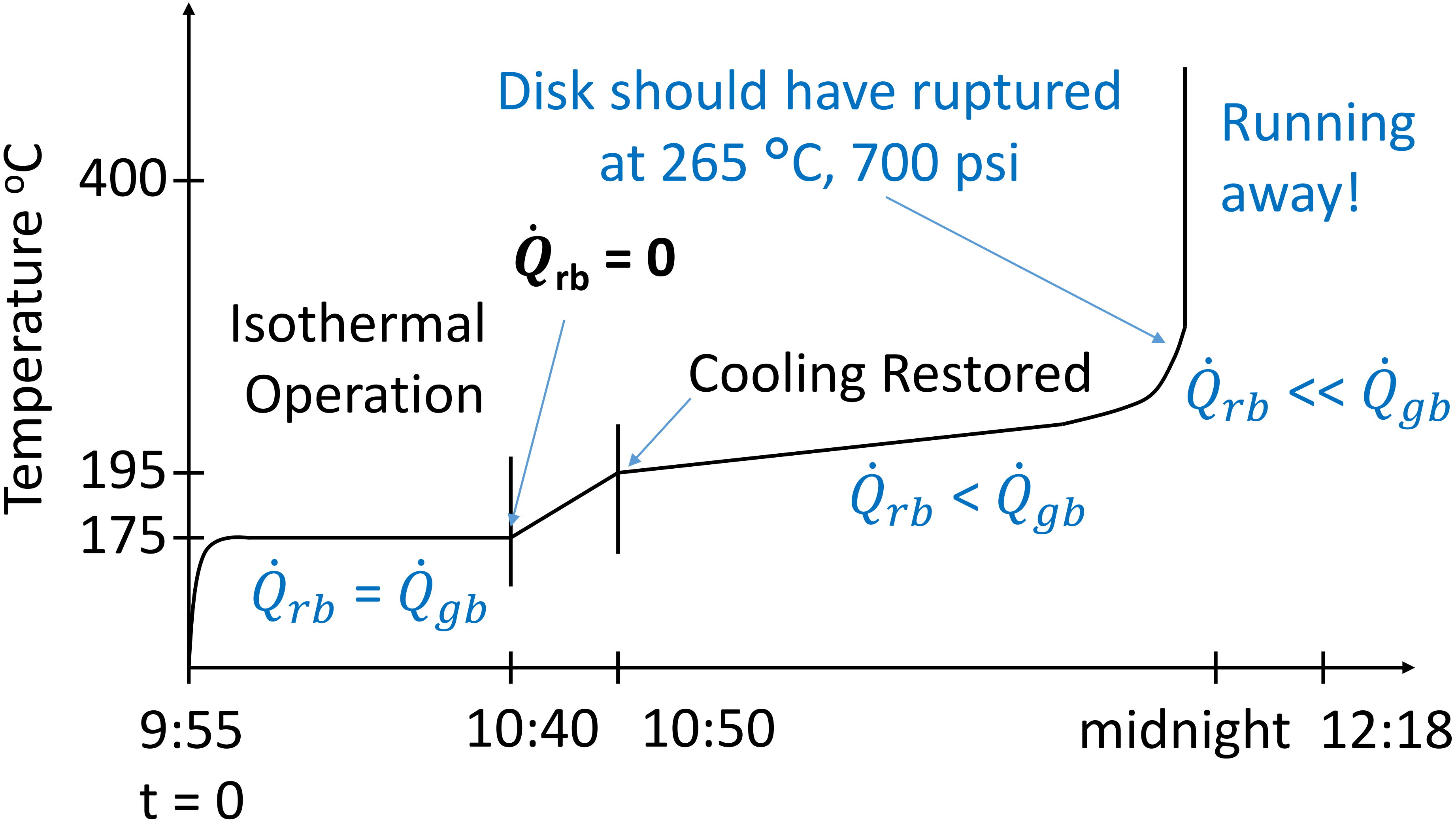
[✓ B) 478 K]

C) 568 K

D) 458 K

*In reality:
$\dot{Q}_{rb}$ linear vs. $\dot{Q}_{gb}$ exponential with T

Temperature profile of nitroaniline batch reactor: Startup to where heat exchanger fails for ~10 min, then after recovery, due to temperature increase reaction rate is too high for heat removal



Isothermal Operation

$\dot{Q}_{rb} = \dot{Q}_{gb}$

$\dot{\boldsymbol{Q}}_{\mathbf{rb}} = \mathbf{0}$

Cooling Restored

$\dot{Q}_{rb} < \dot{Q}_{gb}$

Disk should have ruptured at 265 °C, 700 psi

$\dot{Q}_{rb} << \dot{Q}_{gb}$

Running away!

A pressure relief disk should have ruptured when the temperature reached 265 °C, as the pressure reached 700 psi, but for some reason it did not.

If it had, there would have been a mass flow rate out of the reactor (the reactor emptying through the 2 inch relief orifice) of 830 kg/min.

Under those conditions, even though the generated heat was much higher (higher T, and still sufficient A and B to react):

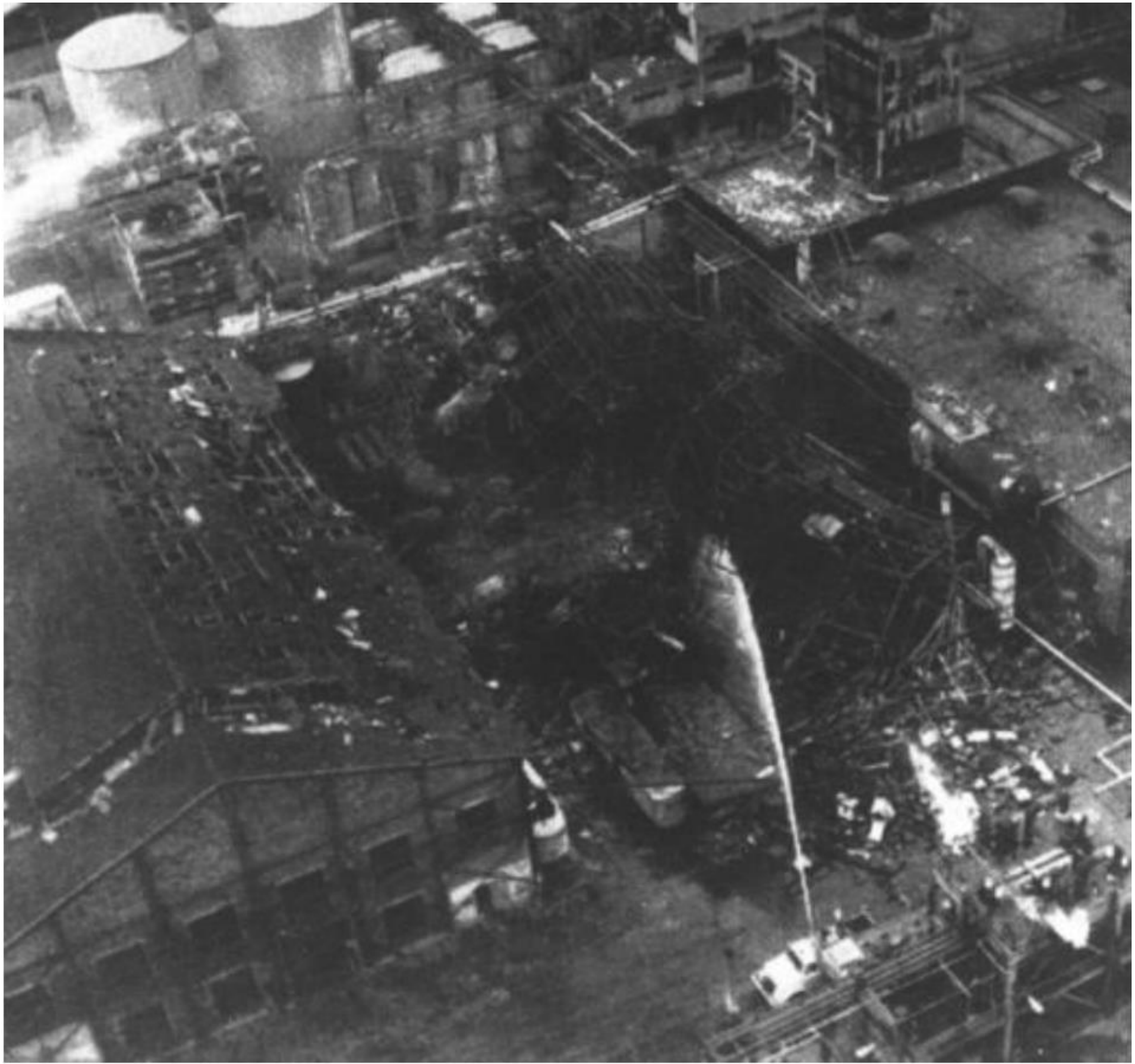
$$(\Delta H_{rxn})(r_A V) = 27{,}460\ kcal/min$$

The removal of heat from the flow rate through the relief outlet would be sufficient to avoid temperature rise:

$$\dot{Q}_{r,\boldsymbol{relief}} \approx 450{,}000 \text{ kcal min}^{-1}$$

Removal here is of water vaporizing as it exits the reactor

The result was an explosion at 12:18. More details will be in your HW8 Safety Module Problem.

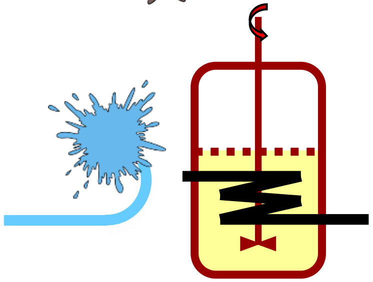


What went wrong?

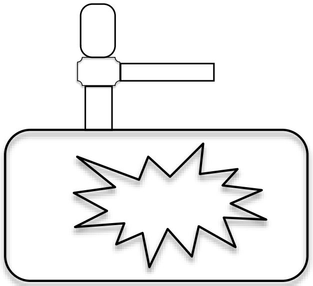
Three things had to occur for the explosion to occur.

1. Tripled Production

2. Heat Exchanger Failure



3.Relief Valve Failure



Discuss with your neighbors:

If our heat generation term is $(\Delta H_{rxn})(r_A V) = -k_1 C_A C_B V \Delta H_{rxn}$, what would have happened if the heat exchanger had failed closer to completion of the reaction?

$$k_1 C_A C_B = k_1 C_{A0}(1 - X) C_{A0}(\theta_B - X)$$

Near the end of rxn, when X is nearly 1, the rate (and thus generation of heat) is much lower

A) Temperature rise would have been the same

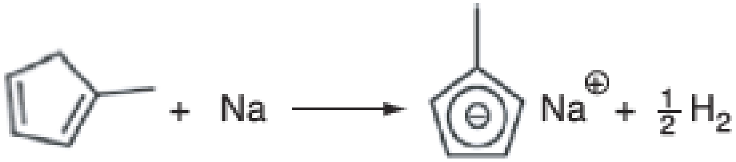
B) Temperature rise would have been higher

[✓ C) Temperature rise would be lower]

D) There would be no T rise at all

Explosion at T2 Laboratories: Safety Module 1

Desired reaction:



Methylcyclopentadiene (MCP) + sodium in solvent of diethylene glycol dimethyl ether to produce sodium methylcyclopentadiene and hydrogen

Previously unknown exothermic reaction (diglyme) catalyzed by sodium

$$CH_3 - O - CH_2 - CH_2 - O - CH_2 - CH_2O - CH_3 \xrightarrow[Na]{} 3H_2 + \mathrm{misc}(l)\,\&\,(s)$$

http://umich.edu/~safeche/courses/ChemicalReactionEngineering.html

View the 10 minute video:

https://www.youtube.com/watch?v=C561PCq5E1g