

**1 Don't say I didn't warn you! (10 pts)**

The enthalpy  $H$  and internal energy  $U$  of a system are related by the expression  $H = U + PV$ .

- 1.1 (10 pts) Starting from this relation, derive an expression for the relationship between the constant pressure molar ( $C_p$ ) and constant volume molar ( $C_v$ ) heat capacities of an ideal gas.

$$C_p = \left( \frac{\partial H}{\partial T} \right)_p \quad C_v = \left( \frac{\partial U}{\partial T} \right)_v$$

$$\begin{aligned} H &= U + PV \\ &= U + RT \quad (\text{ideal gas / per mole}) \end{aligned}$$

$$\left( \frac{\partial H}{\partial T} \right) = \left( \frac{\partial U}{\partial T} \right) + R \left( \frac{\partial T}{\partial T} \right)$$

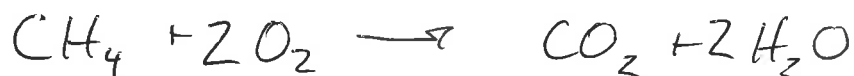
$$C_p = C_v + R$$

## 2 Kaboom! (50 pts)

It's dangerous to put combustible gas mixtures into a closed container. Let's see why. Suppose methane ( $\text{CH}_4$ ) and air (79%  $\text{N}_2$ /21%  $\text{O}_2$ ) are unadvisedly introduced into a closed vessel at  $25^\circ\text{C}$  and 4.00 atm absolute pressure. Your job is to estimate the worst that could come from igniting this mixture. Here's a table of some numbers that might be of some help to you. You can take the heat capacities as constants for the purposes of your estimate and can assume all gases are ideal.

	$\Delta U_f^\circ(25^\circ\text{C})$ ( $\text{kJ mol}^{-1}$ )	$C_p^\circ(25^\circ\text{C})$ ( $\text{J mol}^{-1}^\circ\text{C}^{-1}$ )
$\text{CH}_4(\text{g})$	-72	34
$\text{N}_2(\text{g})$	0	32
$\text{O}_2(\text{g})$	0	33
$\text{H}_2\text{O}(\text{g})$	-241	40
$\text{CO}(\text{g})$	-112	29
$\text{CO}_2(\text{g})$	-393	52
$\text{NO}(\text{g})$	90	30

- 2.1 (5 pts) Write a balanced equation for the complete combustion of methane in air.



- 2.2 (5 pts) Suppose the air is introduced in 30% stoichiometric excess. Determine the initial composition of the gas mixture. Take as a basis 1 mole of methane.

$$n_{\text{CH}_4,0} = 1 \text{ mol}$$

$$\begin{aligned} n_{\text{O}_2,0} &= 2 \cdot n_{\text{CH}_4,0} \cdot 1.3 \\ &= 2.6 \text{ mol} \end{aligned}$$

$$n_{\text{N}_2,0} = n_{\text{O}_2,0} \cdot \frac{0.79}{0.21} = 9.78$$

$$\begin{aligned} &\underline{12.1 \text{ mol}} \\ &13.4 \end{aligned}$$

$$y_{\text{CH}_4,0} = \cancel{0.083} 0.075$$

$$y_{\text{O}_2,0} = \cancel{0.215} 0.194$$

$$y_{\text{N}_2,0} = \cancel{0.702} 0.730$$

- 2.3 (10 pts) Determine the final composition of the gas mixture assuming it accidentally and completely combusted.

complete combustion  $\rightarrow \xi = 1 \text{ mol}$

$$N_{\text{CH}_4} = N_{\text{CH}_4,0} - \xi = 0$$

$$y_{\text{CH}_4} = 0$$

$$N_{\text{O}_2} = N_{\text{O}_2,0} - 2\xi = 0.6$$

$$y_{\text{O}_2} = 0.045$$

$$N_{\text{CO}_2} = \xi = 1.0$$

$$y_{\text{CO}_2} = 0.075$$

$$N_{\text{H}_2\text{O}} = 2\xi = 2.0$$

$$y_{\text{H}_2\text{O}} = 0.149$$

$$N_{\text{N}_2} = N_{\text{N}_2,0} = 9.78$$

$$y_{\text{N}_2} = 0.731$$

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$$13.4 \text{ mol}$$

- 2.4 (5 pts) Suppose, worst case scenario, the vessel is perfectly adiabatic and rigid. Is it appropriate to set up an *energy* or *enthalpy* balance to determine the maximum pressure and temperature? Why?

energy balance appropriate for a constant volume system.

- 2.5 (16 pts) Set up an appropriate energy balance and solve for the final temperature assuming the worst case scenario. Be sure to clearly indicate your balance method, your reference states, and your expressions for enthalpy/energy (as appropriate).

$$\Delta U = 0 \quad (\text{adiabatic \& rigid})$$

1 Use "energy of formation" method

initial

$$\left. \begin{aligned} \hat{U}_{\text{CH}_4}(25^\circ\text{C}, 4 \text{ atm}) &= -72 \\ \hat{U}_{\text{N}_2} &= 0 \\ \hat{U}_{\text{O}_2} &= 0 \end{aligned} \right\} U_{\text{initial}} = -72 \frac{\text{kJ}}{\text{mol}} \cdot 1 \text{ mol} = -72 \times 10^3 \text{ J/mol}$$

final

$$\begin{aligned} \hat{U}_{\text{N}_2}(T, P) &= 0 + \int_{25}^T C_v(T) dT = (T-25) \cdot (32-8.314) \\ &\text{ideal} \rightarrow P \text{ independent} \quad = 23(T-25) \text{ J/mol} \end{aligned}$$

$$\begin{aligned} \hat{U}_{\text{O}_2}(T, P) &= \quad \quad \quad = (T-25) \cdot (32-8.314) \\ &= 24(T-25) \text{ J/mol} \end{aligned}$$

$$\hat{U}_{\text{CO}_2} = -395 + \int_{25}^T C_v(T) dT = -395 + 46(T-25)$$

$$\hat{U}_{\text{H}_2\text{O}} = -241 + \quad \quad \quad = -241 + 32(T-25)$$

$$\begin{aligned} 2 \quad U_{\text{final}} &= 9.78 \cdot 23(T-25) + 0.6 \cdot 24 \cdot (T-25) + \\ &\quad 1.0 \cdot (-395 \times 10^3 + 46(T-25)) + 2.0(-241 \times 10^3 + 32(T-25)) \\ &= 349(T-25) - 877 \times 10^3 \end{aligned}$$

$$349(T-25) - 877 \times 10^3 - (-72 \times 10^3) = 0 \quad \rightarrow$$

$$T = 2330^\circ\text{C}$$

2.6 (5 pts) What is the final pressure in the tank in this worst case scenario?

$$\begin{aligned}P_f &= P_i \cdot \left(\frac{n_f}{n_i}\right) \cdot \left(\frac{T_f}{T_i}\right) \\&= 4 \cdot \left(\frac{13.4}{13.4}\right) \cdot \left(\frac{2330+273}{25+273}\right) \\&= 34.9 \text{ atm}\end{aligned}$$

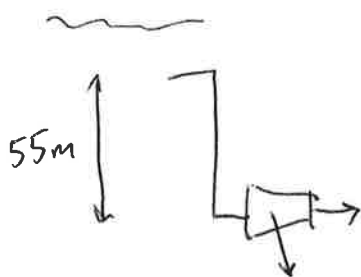
2.7 (4 pts) Give two chemical reasons why the actual maximum temperature in such a catastrophic event will be less than your estimate.

- reaction gives other, less exothermic, products
- heat capacities not constant, increase w/T
- vessel not perfectly adiabatic or rigid

### 3 Mechanical energy balance (30 pts)

Water in a reservoir is used to drive a turbine and make electricity. The turbine is located 55 m below the surface of the reservoir and delivers 0.80 MW of power.

- 3.1 (10 pts) Write an energy balance expression in terms of the required mass flow rate assuming the water exits through a pipe of cross-sectional area  $A$  and neglecting frictional losses.



$$\dot{W}_s = 0.8 \text{ MW}$$

$$\cancel{\Delta \dot{U}} + \Delta \dot{E}_k + \Delta \dot{E}_p = \cancel{\dot{Q}} + \dot{W}_s$$

$$\Delta \dot{E}_p = \dot{m} g \Delta z \quad \Delta \dot{E}_k = \frac{1}{2} \dot{m} (u_f^2 - u_i^2)$$

$$u_f = V_f \cdot \frac{1}{A} = \dot{m} / \rho \cdot A$$

$$\frac{1}{2(\rho A)^2} \dot{m}^3 + \dot{m} g \Delta z = \dot{W}_s$$

- 3.2 (10 pts) Determine the required mass flow rate assuming the water kinetic energy at the exit is negligible.

$$\begin{aligned} \dot{m} &= \dot{W}_s / g \Delta z = \frac{-0.80 \text{ MW}}{9.8 \text{ m/s}^2 \cdot (-55 \text{ m})} \\ &= 1500 \text{ kg/s} \end{aligned}$$

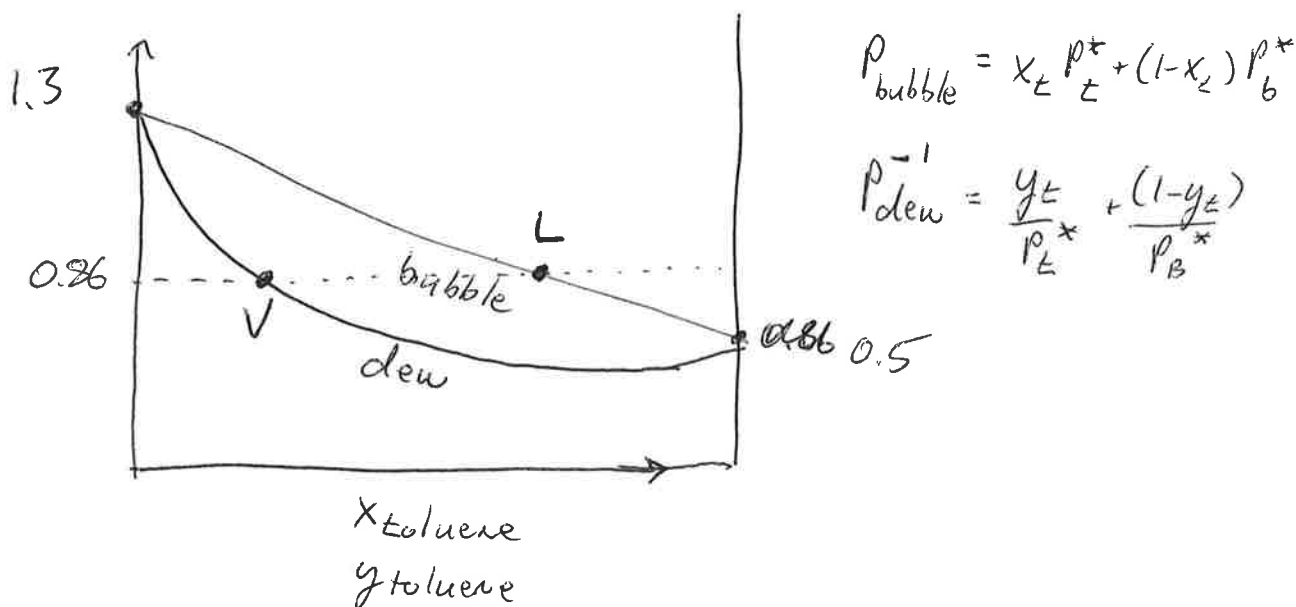
- 3.3 (10 pts) Suppose the actual pipe area is  $A = 0.4 \text{ m}^2$ . What is the impact on the turbine power, assuming the same mass flow rate is as you computed above?

$$\begin{aligned} \dot{W}_s &\rightarrow 0.8 \text{ MW} - \frac{\dot{m}^3}{2(\rho A)^2} \\ &= 0.8 \text{ MW} - \frac{(1500 \text{ kg/s})^3}{2 \cdot (400 \text{ kg/m})^2} \\ &= (0.8 - 0.01) \text{ MW} \quad \text{negligible} \end{aligned}$$

#### 4 Flash dancing (88 pts)

An equimolar (50:50) liquid mixture of benzene and toluene initially at 130°C is to be separated in a continuous flow flash tank heated to 90°C and 0.86 atm. The saturation pressures of benzene and toluene at these conditions are 1.3 and 0.5 atm, respectively, and the liquid and vapor phases in the flash tank can be taken as equilibrated and ideal. The liquid and vapor phases exit through separate streams.

- 4.1 (10 pts) In the space below, sketch a pressure-composition diagram for the benzene-toluene system at 90°C. Be sure to indicate both the bubble and dew lines, and pay attention to the shape of each line.



- 4.2 (10 pts) What is the composition of the exiting liquid phase? Indicate it's location on the diagram above with a dot and an "L".

$$0.86 \text{ atm} = x \cdot 0.5 + (1-x) \cdot 1.3$$

$$= 1.3 - 0.8x$$

$$x = \frac{1.3 - 0.86}{0.8} = 0.55 \quad \text{toluene}$$

$$0.45 \quad \text{benzene}$$

- 4.3 (10 pts) What is the composition of the exiting vapor phase? Indicate it's location on the diagram above with a dot and a "V".

$$\frac{1}{0.86} = \frac{y}{0.5} + \frac{1-y}{1.3}$$

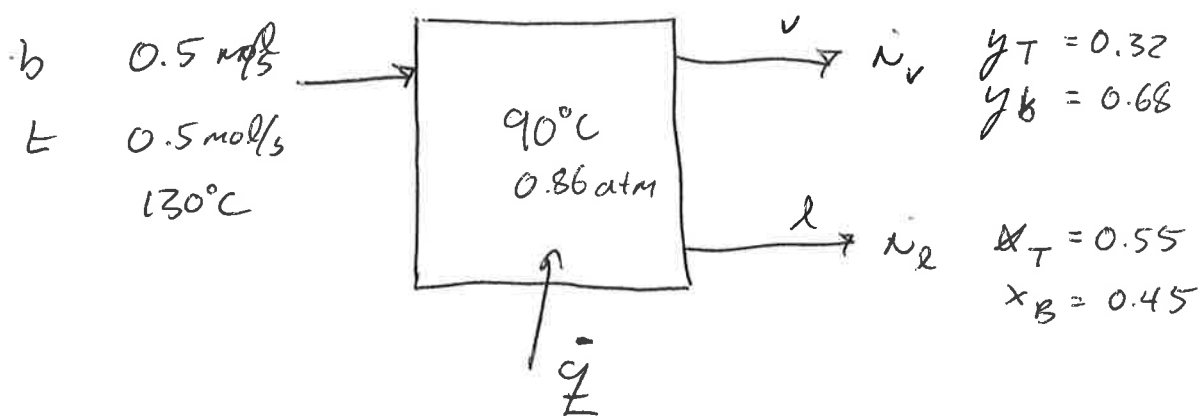
$$\frac{0.5 \cdot 1.3}{0.86} = 1.3y + 0.5(1-y)$$

$$0.755 = 0.8y + 0.5$$

$$y = 0.32 \quad \text{toluene}$$

$$0.68 \quad \text{benzene}$$

- 4.4 (10 pts) Make a process flow chart for the flash tank. Assume a 1 mole/s feed basis and identify all unknown process variables.



unknowns  $q, n_v, n_l$



4.5 (10 pts) Compute the molar flow rates of the exiting liquid and vapor phases.

$$\text{benzene} \quad 0.5 = \dot{n}_v \cdot 0.68 + \dot{n}_l \cdot 0.45$$

$$\text{toluene} \quad 0.5 = \dot{n}_v \cdot 0.32 + \dot{n}_l \cdot 0.55$$

$$\begin{pmatrix} 0.5 \\ 0.5 \end{pmatrix} = \begin{pmatrix} 0.68 & 0.45 \\ 0.32 & 0.55 \end{pmatrix} \begin{pmatrix} \dot{n}_v \\ \dot{n}_l \end{pmatrix}$$

$$\dot{n}_v = 0.22$$

$$\dot{n}_l = 0.78$$

- 4.6 (15 pts) The normal boiling point of benzene is  $80^\circ\text{C}$ ,  $\Delta H_{\text{vap}} = 31 \text{ kJ mol}^{-1}$ , and the heat capacities of liquid and vapor benzene are  $140$  and  $100 \text{ J mol}^{-1}^\circ\text{C}$ , respectively, in the temperature range of interest. Specify a reference state and compute the specific enthalpies of the benzene inlet and outlet streams relative to that reference.

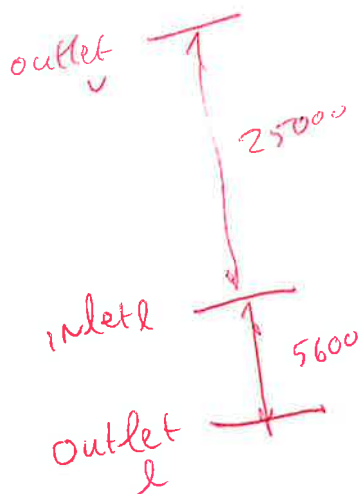
benzene l,  $80^\circ\text{C}$ ,  $\hat{H} = 0$  reference

$$\begin{aligned} \text{inlet} \\ \text{l, } 130^\circ\text{C} \quad \hat{H} &= \int_{80}^{130} 140 \frac{\text{J}}{\text{mol}^\circ\text{C}} dT \\ &= 50 \cdot 140 = 7000 \text{ J/mol} \end{aligned}$$

$$\begin{aligned} \text{outlet} \\ \text{l, } 90^\circ\text{C} \quad \hat{H} &= \int_{80}^{90} 140 dT = 1400 \text{ J/mol} \end{aligned}$$

v,  $90^\circ\text{C}$

$$\begin{aligned} \hat{H} &= \Delta H_{\text{vap}} + \int_{80}^{90} 100 \frac{\text{J}}{\text{mol}^\circ\text{C}} dT \\ &= 31000 + 1000 = 32000 \text{ J/mol} \end{aligned}$$



- 4.7 (15 pts) The specific enthalpies of toluene at the inlet and outlet conditions are given below. At what rate must the flash tank be heated to maintain steady-state operation?

$\hat{H}$ , kJ mol <sup>-1</sup>	
90 °C, l	15
90 °C, v	34
130 °C, l	22

$$\dot{Q} = \Delta \dot{H}$$

$$= \dot{H}_{out} - \dot{H}_{in}$$

$$= 0.22 \cdot (0.32 \cdot 34 + 0.68 \cdot 32)$$

$$+ 0.78 \cdot (0.55 \cdot 15 + 0.45 \cdot 14)$$

$$- 1 \cdot (0.5 \cdot 22 + 0.5 \cdot 7)$$

$$= -0.4 \text{ kJ/s}$$

vapor  
liquid  
liquid  
vapor

- 4.8 With reference back to your phase diagram and energy balance, determine the implications of decreasing the pressure in the flash tank by 0.1 atm on the process variables below. No calculations required; just indicate directional change.

1. (2 pts) the composition of the liquid phase

$x_T$  increases

2. (2 pts) the composition of the vapor phase

$y_T$  increases

3. (2 pts) the ratio of vapor to liquid phase

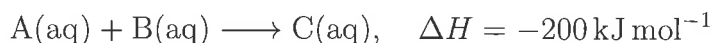
↑ vapor

4. (2 pts) the required heating rate

$\dot{Q}$  ↑

## 5 Semi-batch reaction (15 pts)

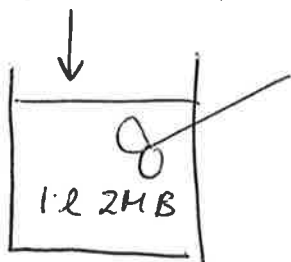
Aqueous A and B react to C according to the reaction:



An adiabatic, well-mixed semi-batch reactor contains 1.0 L of 2.0 mol L<sup>-1</sup> B. A 3.0 mol L<sup>-1</sup> solution of A is introduced into the vessel at a rate solutions of 0.10 L min<sup>-1</sup>. Both solutions start at 25°C, and the heat capacities and densities of all solutions are the same as that of ambient water.

- 5.1 (15 points) At what time does the temperature inside the reactor reach its maximum, and what is that maximum temperature?

3 M A 0.1 L/min



$$V = V_0 + 0.1 t \quad \text{L}$$

$$m = m_0 + 0.1 \rho \cdot t$$

$$\xi = \frac{3 \text{ mol/L}}{\text{L}} \cdot \frac{0.1 \text{ L}}{\text{min}} \cdot t = \frac{0.3}{\text{min}} \cdot t$$

$$\xi_{\text{max}} = 2.0 \rightarrow t_{\text{max}} = \underline{6.7 \text{ min}}$$

adiabatic

$$\Delta H = 0 = H(t) - H(0)$$

$$H(t) = H(0) + \xi(\Delta H_{\text{rxn}}) + (\cancel{m_0} + m) C_p \Delta T$$

$$= H(0) + 0.3 \cdot t \cdot \Delta H + \cancel{0.1 \rho \cdot t} \cdot \Delta T \cdot C_p$$

$$C_p (m_0 + 0.1 \rho t) \cdot \Delta T = 0$$

$$\Delta T = - \frac{0.3 t \cdot \Delta H}{m_0 + 0.1 \rho t}$$

$$= - \frac{0.3 \cdot 6.7 \cdot (-200 \text{ kJ})}{\frac{4.184 \text{ kJ}}{\text{kg}} \left( 1 \text{ kg} + 0.1 \frac{\text{L}}{\text{min}} \cdot \frac{\text{kg}}{\text{L}} \cdot 6.7 \text{ min} \right)}$$

$$= 57$$

$$T_{\text{Anax}} = 25 + 57 = 82^\circ \text{C}$$