

P6.1

$$100 \text{ kcal} = 418.4 \text{ kJ} = 396.6 \text{ Btu.}$$

$$\frac{125,000 \text{ kJ/gallon gasoline}}{418.4 \text{ kJ/apple}} \approx 300 \text{ apples/gallon gasoline}$$

P6.2

Hairdryer: 1500 W

$$1500 \text{ W} \times \frac{1.341 \text{ hp}}{1000 \text{ W}} = 2.01 \text{ hp}$$

$$1500 \text{ W} \times \frac{1 \text{ kW}}{1000 \text{ W}} \times \frac{0.239 \text{ kcal/s}}{1 \text{ kW}} \times \frac{60 \text{ s}}{\text{min}} = 21.5 \text{ kcal/min}$$

$$1500 \text{ W} \times \frac{1 \text{ kW}}{1000 \text{ W}} \times \frac{3412 \text{ Btu/h}}{1 \text{ kW}} = 5118 \text{ Btu/h}$$

$$\text{Lightbulb} = 100 \text{ W} = 0.1341 \text{ hp} = 0.1 \text{ kJ/s} = 1.43 \text{ kcal/min} = 341.2 \text{ Btu/h}$$

$$\text{Two-way radio transmitter} = 500 \text{ mW} = 0.5 \text{ W} = 6.705 \times 10^{-4} \text{ hp} = 5 \times 10^{-4} \text{ kJ/s} = 0.00717 \text{ kcal/min} = 1.706 \text{ Btu/h}$$

P6.3

$$\frac{\$2.00}{125,000 \text{ kJ}} \times \frac{1 \text{ kJ}}{0.9478 \text{ Btu}} = \$16.88/\text{million Btu}$$

Price is closer to electricity than to coal. Refining, distribution costs and taxes are significant.

P6.4

$$305 \text{ gal} \left(\frac{0.877 \text{ g}}{\text{cm}^3} \right) \left(\frac{1000 \text{ cm}^3}{0.26417 \text{ gal}} \right) \left(\frac{\text{lb}}{454 \text{ g}} \right) = 2230 \text{ lb}$$

$$72 \text{ lbmol} \left[0.24 \times \frac{46.07 \text{ lb}}{\text{lbmol}} + 0.76 \times \frac{18.016 \text{ lb}}{\text{lbmol}} \right] = 1782 \text{ lb}$$

Total mass = 2230 + 1782 = 4012 lb (mass is the same on Earth and on Phobos)

Total weight = 4012 lb_f on Earth

$$\text{Total weight} = 4012 \text{ lb} \left(\frac{3.78 \text{ ft/s}^2}{32.174 \text{ lb ft/lb}_f \text{ s}^2} \right) = 471 \text{ lb}_f \text{ on Phobos.}$$

P6.5

$$1 \text{ oxpower} = \frac{1000 \text{ lb} \times 200 \text{ ft}}{13 \text{ min}} \times \frac{\text{lb}_f}{\text{lb}} = 15385 \frac{\text{lb}_f \text{ ft}}{\text{min}} \times \frac{\text{hp}}{33000 \text{ ft lb}_f / \text{min}} = 0.47 \text{ hp}$$

P6.6

$$\left(\frac{125000 \text{ kJ}}{\text{gal}} \right) \left(\frac{1 \text{ gal}}{20 \text{ mi}} \right) (5 \text{ mi}) \left(\frac{1 \text{ kcal}}{4.184 \text{ kJ}} \right) \left(\frac{1 \text{ apple}}{100 \text{ kcal}} \right) = 75 \text{ apples}$$

P6.7

Light bulb = 100 W

$$100 \text{ W} = \frac{1 \text{ W}}{1000 \text{ mW}} \times \frac{96.4 \text{ mW}}{\text{cm}^2} \times 0.017 \times A$$

$$A = 61,000 \text{ cm}^2 = 66 \text{ ft}^2$$

Hair dryer = 1500 W

$$1500 \text{ W} = \frac{1 \text{ W}}{1000 \text{ mW}} \times \frac{96.4 \text{ mW}}{\text{cm}^2} \times 0.017 \times A$$

$$A = 915,000 \text{ cm}^2 = 984 \text{ ft}^2$$

(A typical suburban American home is roughly 2000 ft²).

P6.8

Skier goes from 0 to 60 mph:

$$\frac{60 \text{ mi}}{\text{h}} \times \frac{\text{h}}{3600 \text{ s}} \times \frac{5280 \text{ ft}}{\text{mi}} = \frac{88 \text{ ft}}{\text{s}}$$

$$\Delta E_k = \frac{m(v_2^2 - v_1^2)}{2} = \frac{100 \text{ lb}}{2} \times \left[\left(\frac{88 \text{ ft}}{\text{s}} \right)^2 - 0^2 \right] = 387,200 \text{ lb} \cdot \text{ft}^2/\text{s}^2 \times \frac{\text{lb}_f}{32.174 \text{ lb} \cdot \text{ft}/\text{s}^2} = 12034 \text{ ft} \cdot \text{lb}_f$$

Skier drops 1200 ft in elevation:

$$\Delta E_p = mg(h_2 - h_1) = 100 \text{ lb} \times 32.174 \frac{\text{ft}}{\text{s}^2} \times (0 - 1200 \text{ ft}) \times \frac{\text{lb}_f}{32.174 \text{ lb} \cdot \text{ft}/\text{s}^2} = -120,000 \text{ ft} \cdot \text{lb}_f$$

Skis generate frictional loss at a rate of 3 100- watt light bulbs per ski, over a total of 32 seconds:

$$Q = -2 \times 3 \times 100 \frac{\text{J}}{\text{s}} \times \frac{737.6 \text{ ft} \cdot \text{lb}_f}{1000 \text{ J}} \times 32 \text{ s} = -14162 \text{ ft} \cdot \text{lb}_f$$

P6.9

$$E_{k2} - E_{k1} = \frac{m}{2} (v_2^2 - v_1^2) = \frac{3 \text{ kg}}{2} (100^2 - 11,000^2) \frac{\text{m}^2}{\text{s}^2} \times \frac{\text{J}}{\text{kg m}^2/\text{s}^2} \times \frac{\text{kJ}}{1000 \text{ J}} = -181,500 \text{ kJ}$$

Meteorite heats up.

P6.10

Assume at 1 bar. At 50°C, $\hat{H} = 209.46 \text{ kJ/kg}$ and at 99.606°C and liquid,

$\hat{H} = 417.50 \text{ kJ/kg}$. By linear interpolation, at 75°C:

$$\frac{\hat{H} - 209.46 \text{ kJ/kg}}{417.5 - 209.46 \text{ kJ/kg}} = \frac{75 - 50}{99.6 - 50}$$

$$\hat{H} = 314.32 \text{ kJ/kg}$$

The change in enthalpy associated with condensing steam at 99.6°C is 2674.9 - 417.5 = 2257.4 kJ/kg. (Assume same at 100°C.). Therefore,

$$\frac{2257.4}{314.32 - 209.46} = 21.5 \text{ kg water can be heated from 50 to 75°C for each 1 kg steam condensed.}$$

P6.11

At 213 K, 0.1 bar, $\hat{H} = -530 \text{ kJ/kg}$. At 253 K, 1 bar, $\hat{H} = -300 \text{ kJ/kg}$.

$$\Delta\hat{H} = \hat{H}_2 - \hat{H}_1 = -300 - (-530) = +230 \text{ kJ/kg solution}$$

P6.12

Assume coffee has same heat capacity as water or about 4 J/g °C. Assume an 8 oz cup of coffee or about 1/2 lb or about 225 g. Assume room temperature is about 20°C.

$$Q = mC_p(T_2 - T_1) \approx 225 \text{ g} \times 4 \text{ J/g } ^\circ\text{C} \times (20^\circ\text{C} - 70^\circ\text{C}) \approx -45,000 \text{ J}$$

There are 4.184 J/cal and $9.47817 \times 10^{-4} \text{ Btu/J}$, so

$$Q \approx -\frac{45,000 \text{ J}}{4.184 \text{ J/cal}} \approx -11,000 \text{ cal}$$

$$Q \approx -45,000 \text{ J} \times 9.47817 \times 10^{-4} \text{ Btu/J} \approx -43 \text{ Btu}$$

P6.13

With Freon R-22 $Q = mC_p(T_2 - T_1) = 100 \text{ J} = 10 \text{ g}(0.6 \text{ J/g})(T_2 - T_1)$
 $(T_2 - T_1) = 16.7^\circ\text{C}$

With water $Q = mC_p(T_2 - T_1) = 100 \text{ J} = 10 \text{ g}(4 \text{ J/g})(T_2 - T_1)$
 $(T_2 - T_1) = 2.5^\circ\text{C}$

P6.14

For CO₂

$$C_p = 19.8 + 0.07344T - 5.602 \times 10^{-5}T^2 + 1.17115 \times 10^{-8}T^3$$

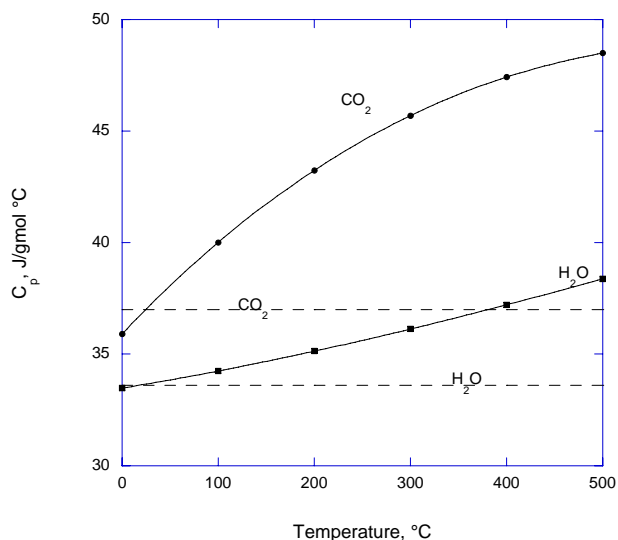
For water vapor

$$C_p = 32.24 + 0.001924T + 1.0552 \times 10^{-5}T^2 - 3.596 \times 10^{-9}T^3$$

with T in K and C_p in J/gmol K.

Values were calculated at increments of 100°C from 100 to 500 °C (373 – 973 K) in a spreadsheet, and the results were plotted.

T	100	200	300	400	500
C_p, CO_2 (J/gmol°C)	40.01	43.24	45.69	47.42	48.50
$C_p, \text{H}_2\text{O}$ (J/gmol°C)	34.24	35.13	36.13	37.22	38.37



The heat capacity increases significantly with temperature (solid lines). The dashed lines indicate the approximate C_p values given in Table B.17. The approximate values are useful around room temperature but become increasingly in error as the temperature increases.

The rule of thumb (p. 523) states that C_p of a gas is about 1 J/g °C. Converting to molar basis, this would be 44 J/gmol °C for CO_2 and 18 J/gmol °C for H_2O . The estimate for CO_2 isn't too bad; water is an anomaly even in the vapor phase.

P6.15

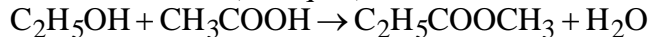
From Table B.21, for citric acid dissolving in water at 25°C, the enthalpy of solution is defined as *negative* if heat is *absorbed* (endothermic). (This is the opposite of the definition in Table B.22). The enthalpy of a citric acid solution is greater than the enthalpy of the citric acid and water separately, if the temperature is kept constant .

$$\Delta H = m_{\text{solute}} (-\Delta \hat{H}_{\text{soln}}) = (1 \text{ gmol citric acid}) \times (22.598 \text{ kJ/gmol solute}) = +22.598 \text{ kJ}$$

If the beaker is adiabatic, the solution will feel cool to the touch, because the temperature will drop a bit.

P6.16

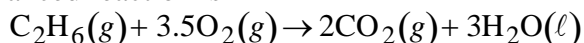
The balanced reaction is (all liquid)



$$\Delta \hat{H}_r^\circ = \sum_i \nu_i \Delta \hat{H}_{f,i}^\circ = (-1)(-277.61) + (-1)(-486.18) + (-463.3) + (-285.84) = 14.65 \text{ kJ/gmol}$$

P6.17

The balanced reaction is



$$\Delta \hat{H}_r^\circ = \sum_i \nu_i \Delta \hat{H}_{f,i}^\circ = (-1)(-83.82) + (-3.5)(0) + (2)(-393.5) + 3(-285.84) = -1560.7 \text{ kJ/gmol}$$

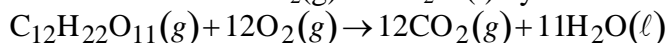
In Table B.3 $\Delta \hat{H}_c^\circ = -1428.6 \text{ kJ/gmol}$ for combustion of ethane, but this is with water vapor as the product. With liquid water as the product,

$$\Delta \hat{H}_c^\circ = -1428.6 + 3(-44.0) = 1560.6 \text{ kJ/gmol}$$

which is identical to the value obtained above.

P6.18

Sucrose is metabolized to $\text{CO}_2(g)$ and $\text{H}_2\text{O}(\ell)$ by oxidation.



The energy released is

$$\Delta \hat{H}_r^\circ = (-1)(-2221) + (-12)(0) + (12)(-393.5) + 11(-285.84) = -5645 \text{ kJ/gmol}$$

The molar mass of sucrose is 342 g/gmol. There are

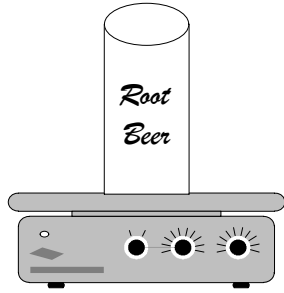
$$\frac{5645 \text{ kJ/gmol}}{342 \text{ g/gmol}} \times \frac{0.2389 \text{ kcal}}{\text{kJ}} = 3.94 \text{ kcal/g}$$

or, about 83 kcal in a 21 g hard candy. (A diet “calorie” is actually a kcal. Carbohydrates and proteins have about 4 “calories” per gram. Fats and oils have about 9 “calories” per gram.)

P6.19

(a) As the can is being heated, just up to but not including the time when steam is emitted, the energy balance is simple: no mass enters or leaves the system, there is a heat input but no work term, and the internal energy of the system changes. We write an integral energy balance because we are interested in what happens over a specified time interval.

$$U_{sys,f} - U_{sys,0} = Q$$



For this case, $Q > 0$ and $W_s = 0$. (At the point steam starts to leave, there will be an additional $\dot{m}_{out}\hat{H}_{out}$ to consider.)

(b) When the can is suddenly inverted into a bowl full of ice-cold water, the steam inside the can rapidly condenses and the volume of the contents decreases. No air enters the can because the hole is plugged by the ice-cold bath. The can implodes. There is no mass entering or leaving, there is clearly a heat output term, and there is also a work term as the system boundary is pushed on by the external atmosphere.

$$U_{sys,f} - U_{sys,0} = Q + W_s$$

with

$$Q < 0 \text{ and } W_s > 0.$$

P6.20

(a) System is the contents of the turbine. The inlet and outlet ports are at the same height, so there is no change in potential energy. We will assume no change in velocity and hence no change in kinetic energy (lacking any other information). There is clearly work output, and it is stated that there is heat output. Mass enters and leaves the system. The system is assumed to be at steady state.

$$\dot{m}_{out}\hat{H}_{out} - \dot{m}_{in}\hat{H}_{in} = \dot{Q} + \dot{W}_s$$

where “out” and “in” refer to the steam exiting and entering the system.

$$\dot{Q} < 0 \text{ and } \dot{W}_s < 0$$

(b) We assume steady state operation and choose as our system the contents of the material between inlet and outlet pipes. There is no change in velocity or elevation, so no change in kinetic or potential energy. There is some heat added, but no work term (no mechanical equipment).

$$\dot{m}_{out}\hat{H}_{out} - \dot{m}_{in}\hat{H}_{in} = \dot{Q}, \text{ with } \dot{Q} > 0$$

(c) The system is the water in the sluice gate and turbine. There are no phase, pressure, or temperature changes in the water, nor any change in fluid velocity, so there is no change in enthalpy or kinetic energy of the streams entering and leaving, but there is a change in elevation (and therefore in potential energy). There is a work output but no significant heat term. Assuming steady state

$$\dot{m}_{out}\hat{E}_{p,out} - \dot{m}_{in}\hat{E}_{p,in} = \dot{W}_s, \text{ with } \dot{W}_s < 0$$

(d) The system is the contents of the oil pipeline (the crude oil). There is an elevation gain, no velocity change, and a pump (work). There is also heat lost to the environment. We will assume no significant changes in temperature, as it is stated that any heat generated by friction is lost to the environment. Assuming steady state,

$$\dot{m}_{out} \hat{E}_{p,out} - \dot{m}_{in} \hat{E}_{p,in} = \dot{Q} + \dot{W}_s, \text{ with } \dot{Q} < 0 \text{ and } \dot{W}_s > 0$$

(e) The system is the reactor and its contents. Lacking any other information, we'll assume the reactor is adiabatic (insulated), so there is no heat input. With chemical reactions, we can generally ignore any minor changes in potential or kinetic energy. There is no mechanical equipment. Assuming steady state, and that only ammonia exits the reactor:

$$\dot{m}_{N_2,in} \hat{H}_{N_2,in} + \dot{m}_{H_2,in} \hat{H}_{H_2,in} = \dot{m}_{NH_3,out} \hat{H}_{NH_3,out} \text{ with } \dot{Q} = 0 \text{ and } \dot{W}_s = 0$$

(f) The system is the water in the pipe. There is clearly an elevation change, no significant temperature or pressure changes, no work term, and no significant heat term. If the system is at steady state, there must be a kinetic energy increase to balance the potential energy decrease, since there are no other changes. The energy balance is

$$\dot{m}_{out} (\hat{E}_{p,out} + \hat{E}_{k,out}) = \dot{m}_{in} (\hat{E}_{p,in} + \hat{E}_{k,in}), \text{ with } \dot{Q} = 0 \text{ and } \dot{W}_s = 0$$

(There is some friction, but we don't know if that would go to heat up the water in the pipe or be lost to the environment. So we neglect.)

(g) The bread dough is the system. As the yeast digest the sugar, CO₂, water, ethanol, lactic acid, and other organic compounds are produced. There is a change in the internal energy of the dough. If all the CO₂ is trapped in the dough, the dough volume increases, and the dough does work on the surroundings. It is unclear whether the dough is the same temperature as the surroundings or not. If at the same temperature, there is no heat term. The balance is

$$\frac{dU_{sys}}{dt} = \dot{Q} + \dot{W}_s \text{ with } \dot{W}_s < 0 \text{ and the sign of } \dot{Q} \text{ uncertain.}$$

(h) This is similar to (e), except, since the reaction happens in a furnace there is heat input. We also do not know anything about the extent of reaction. The energy balance at steady state is

$\dot{m}_{out} \hat{H}_{out} - \dot{m}_{in} \hat{H}_{in} = \dot{Q}$ with $\dot{W}_s = 0$ and $\dot{Q} > 0$. All compounds in the inlet and outlet streams are considered in the enthalpy calculation.

(i) If the contents of the cup serves as the system and the cup is very well insulated, the energy balance is

$$\frac{dU_{sys}}{dt} = \dot{m}_{milk,in} \hat{H}_{milk,in}$$

(A negative heat term is required if the cup is not well insulated.)

(j) If the system is the contents of the beaker, assuming the beaker is not well insulated,

$$\frac{dU_{sys}}{dt} = \dot{m}_{water,in} \hat{H}_{water,in} + \dot{Q}$$

Since there is a large exothermic enthalpy of solution associated with this system (as well as a serious safety risk – one should always “do as you oughta, add acid to watah!” (said with a Boston accent)), the temperature in the beaker will temporarily increase and there will be heat output, so $\dot{Q} < 0$.

(k) The student is the system. When the student sleeps, there is no work being done (unless you count breathing), but there is heat loss from the student to the surroundings (unless the room is *very* warm). There is mass exchange with the surroundings, as air is taken in and CO₂ and water are exhaled. Assuming steady state (i.e., the student is always sleeping),

$$\dot{m}_{out} \hat{H}_{out} - \dot{m}_{in} \hat{H}_{in} = \dot{Q} \text{ with } \dot{W}_s = 0 \text{ and } \dot{Q} < 0.$$

P6.21

(a) By linear interpolation we find the enthalpy of liquid water at 1 bar and 75°C

$$\frac{\hat{H} - 209.46 \text{ kJ/kg}}{417.5 - 209.46 \text{ kJ/kg}} = \frac{75 - 50}{99.6 - 50}$$

$$\hat{H} = 314.3 \text{ kJ/kg}$$

At 10 bar and 200°C,

$$\hat{H} = 2828.3 \text{ kJ/kg}$$

The change in enthalpy is therefore 2828.3 – 314.3 or 2514 kJ/kg.

(b) (i) from 75°C to 99.6°C, liquid at 1 bar

$$\Delta \hat{H} = 417.50 - 314.3 = 103.2 \text{ kJ/kg}$$

(ii) from liquid to vapor at 99.6°C and 1 bar

$$\Delta \hat{H} = 2674.9 - 417.50 = 2257.4 \text{ kJ/kg}$$

(iii) from 99.6°C to 200°C as vapor at 1 bar

$$\Delta \hat{H} = 2875.5 - 2674.9 = 200.6 \text{ kJ/kg}$$

(iv) from 1 bar to 10 bar at 200 °C and vapor

$$\Delta \hat{H} = 2828.3 - 2875.5 = -47.2 \text{ kJ/kg}$$

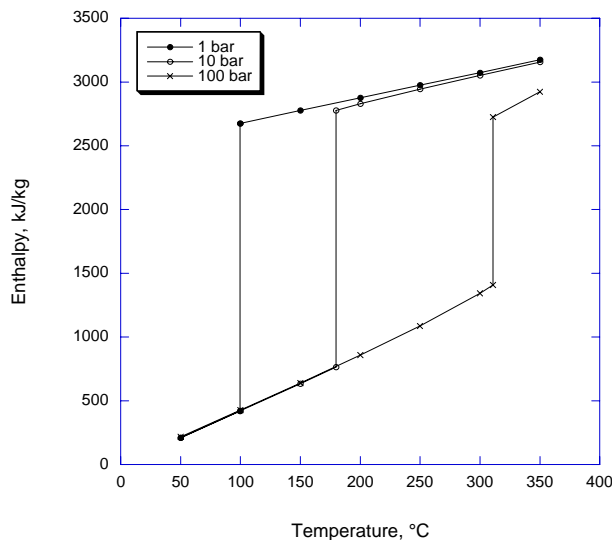
The total change in enthalpy for these four steps is

$$\Delta \hat{H} = 103.2 + 2257.4 + 200.6 - 47.2 = 2514 \text{ kJ/kg}$$

Same answer.

P6.22

The data were plotted as enthalpy vs. temperature.



(a) and (b) To determine C_p , we fit a straight line to the data in the region (vapor or liquid) that we are interested in. The slope is the heat capacity (recall that C_p is the change in enthalpy with a change in temperature, with constant pressure and phase.) Kaleidagraph (see Appendix A), Excel, or other graphing programs can be used to find a linear regression fit to the data.

Results:

Pressure	C_p , liquid, kJ/kg°C	C_p , steam, kJ/kg°C	$\Delta\hat{H}_{vap}$, kJ/kg
1 bar	4.19	1.996	2257.4
10 bar	4.25	2.23	2014.58
100 bar	4.55	5.09	1317.4

C_p for liquid water changes just slightly with pressure while C_p for steam changes substantially; keeping in mind that the temperature range over which water remains a liquid changes as the pressure changes, this may account for at least part of what we observe. For liquids it is generally safe to assume a constant heat capacity except for very accurate work. For vapors and gases, this is less safe, especially if the temperature is changing by a few hundred degrees.

The enthalpy of vaporization decreases pretty quickly with increasing pressure (and the corresponding increase in temperature). As the pressure approaches the critical pressure, the enthalpy of vaporization approaches zero. This is because with the approach to critical conditions, vapor and liquid phases become indistinguishable.

P6.23

With model equations, we first calculate the change in enthalpy due to the change in pressure at constant temperature

$$\Delta\hat{H} = \hat{V}\Delta P = \left(0.00101 \text{ m}^3/\text{kg}\right) \times (10 - 1 \text{ bar}) \times \frac{10^5 \text{ N/m}^2}{\text{bar}} \times \frac{\text{kJ}}{1000 \text{ N m}} = 0.91 \text{ kJ/kg}$$

then the change in enthalpy due to the change in temperature at constant pressure

$$\Delta\hat{H} = C_p\Delta T = \frac{(75.4 \text{ J/gmol } ^\circ\text{C})}{18 \text{ g/gmol}} \times (100 - 50^\circ\text{C}) \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{\text{kJ}}{1000 \text{ J}} = 209.4 \text{ kJ/kg}$$

The total change in enthalpy is $209.4 + 0.91 = 210.31$, virtually all of it due to the change in temperature.

From the steam table

$$\Delta\hat{H} = 419.8 - 209.46 = 210.34 \text{ kJ/kg}$$

The numbers are very close!

P6.24

(a) From steam table, the enthalpy at 320°C is found by linear interpolation

$$\hat{H}_{320} = 3074.6 + \frac{20}{50}(3175.8 - 3074.6) = 3115.1 \text{ kJ/kg}$$

The total enthalpy change due to increasing the temperature from 100 to 320°C is

$$\Delta H = m\Delta\hat{H} = (20 \text{ kg})(3115.1 - 2675.8 \text{ kJ/kg}) = 8786 \text{ kJ/kg}$$

(b) Using the approximate heat capacity of $33.6 \text{ J/gmol } ^\circ\text{C}$ from Table B.17

$$\Delta H = m\Delta\hat{H} = (20 \text{ kg})(33.6 \text{ kJ/kgmol } ^\circ\text{C})(320 - 100^\circ\text{C})(1 \text{ kgmol}/18 \text{ kg}) = 8213 \text{ kJ}$$

or about 6% too low.

(c) Using the polynomial expression from Table B.17

$$\Delta H = \left(\frac{20 \text{ kg}}{18 \text{ kg/kgmol}}\right) \int_{373}^{593} (32.24 + 0.001924T + 1.055 \times 10^{-5}T^2 - 3.596 \times 10^{-9}T^3) dT = 8616 \text{ kJ}$$

which is within 2% of the true answer.

P6.25

To freeze water: first we cool liquid water from 20°C to 0°C , then we change phase from liquid to solid:

$$\Delta H = m\Delta\hat{H} = \left(\frac{1 \text{ kg}}{18 \text{ kg/kgmol}}\right) [(75.4 \text{ kJ/kgmol } ^\circ\text{C})(0 - 20^\circ\text{C}) + (-6008 \text{ kJ/kgmol})] = -418 \text{ kJ}$$

To evaporate 1 kg of water: first we heat liquid water from 20°C to 100°C, then we change phase from liquid to vapor at 100°C:

$$\Delta H = m\Delta\hat{H} = \left(\frac{1 \text{ kg}}{18 \text{ kg/kgmol}}\right) \left[(75.4 \text{ kJ/kgmol } ^\circ\text{C})(100 - 20^\circ\text{C}) + (40650 \text{ kJ/kgmol}) \right] = 2593 \text{ kJ}$$

It takes about 6-fold more kJ to evaporate than to freeze water. Does this translate into savings in energy costs?

To reach 0°C we need a refrigerant. Choosing the refrigerant operating at -20°C, we estimate energy costs for freezing 1000 kg (one metric ton) at

$$1000 \text{ kg} \times 418 \text{ kJ/kg} \times \$32/10^6 \text{ kJ} = \$13.38$$

Evaporating the water can be done with low pressure steam, if we go with the higher estimate from the data on p. 500:

$$1000 \text{ kg} \times 2593 \text{ kJ/kg} \times \$3/10^6 \text{ kJ} = \$7.78$$

Freezing is about twice as expensive as evaporation.

P6.26

(a) kinetic energy change:

$$\begin{aligned} \Delta E_k &= \frac{m}{2} (v_2^2 - v_1^2) = \frac{1 \text{ gmol} \times 18 \text{ g/gmol}}{2} \left((100 \text{ km/h})^2 - (0 \text{ km/h})^2 \right) \\ &= \left(90000 \frac{\text{g km}^2}{\text{h}^2} \right) \times \left(\frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{10^6 \text{ m}^2}{\text{km}^2} \times \frac{\text{h}^2}{3600^2 \text{ s}^2} \times \frac{\text{J}}{\text{kg m}^2/\text{s}^2} \right) = 6.9 \text{ J} \end{aligned}$$

(b) potential energy change:

$$\begin{aligned} \Delta E_p &= mg(h_2 - h_1) = (1 \text{ gmol} \times 18 \text{ g/gmol}) (9.8066 \text{ m/s}^2) (100 \text{ m} - 0 \text{ m}) \\ &= \left(17651 \frac{\text{g m}^2}{\text{s}^2} \right) \times \left(\frac{1 \text{ kg}}{1000 \text{ g}} \times \frac{\text{J}}{\text{kg m}^2/\text{s}^2} \right) = 17.6 \text{ J} \end{aligned}$$

(c) internal energy change due to pressure change (from steam table):

$$\Delta U = m\Delta\hat{U} = 18 \text{ g} \times (2506.2 - 2515.5 \text{ J/g}) = -167 \text{ J}$$

(d) internal energy change due to temperature change (from liquid heat capacity):

$$\Delta U = nC_v\Delta T = 1 \text{ gmol} \times 75.4 \text{ J/gmol } ^\circ\text{C} \times (100 - 0^\circ\text{C}) = 7540 \text{ J}$$

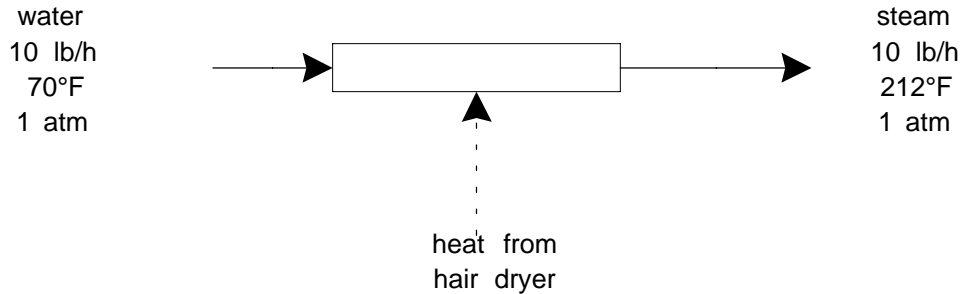
(e) internal energy change due to reaction (reverse of formation reaction)

$$\begin{aligned} \Delta\hat{U}_r &\cong \Delta\hat{H}_r - RT\Delta n_r = (285.84 \text{ kJ/gmol})(1000 \text{ J/kJ}) - (8.3144 \text{ J/gmol K})(298 \text{ K})(+0.5 \text{ gmol}) = 284,600 \text{ J/gmol} \\ \Delta U_r &= n\Delta\hat{U}_r = 284,600 \text{ J} \end{aligned}$$

(f) energy change due to nuclear reaction

$$\Delta E = (\Delta m)c^2 = (18 \text{ g})\left(2.99792 \times 10^8 \text{ m/s}\right)^2 \left(\frac{1 \text{ kg}}{1000 \text{ g}}\right) \left(\frac{\text{J}}{\text{kg m}^2/\text{s}^2}\right) = 1.6 \times 10^{15} \text{ J}$$

P6.27



The system is the contents of the pipe. The mass balance is obvious as long as steady-state operation is assumed. The energy balance equation simplifies to:

$$\dot{m}_{out}\hat{H}_{out} - \dot{m}_{in}\hat{H}_{in} = \dot{Q}$$

The inlet temperature is 21°C and the outlet is 100°C. We construct a path from inlet to outlet by (a) heating liquid water from 21°C to 100°C at 1 atm, and (b) vaporizing water to steam at 100°C and 1 atm.

$$\dot{m}_{out}\hat{H}_{out} - \dot{m}_{in}\hat{H}_{in} = \dot{m}(\hat{H}_{out} - \hat{H}_{in}) = \dot{m}(C_p(T_{out} - T_{in}) + \Delta\hat{H}_{vap}) = \dot{Q}$$

$$\dot{Q} = \left(\frac{10 \text{ lb/h} \times 454 \text{ g/lb}}{18 \text{ g/gmol}}\right) [(75.4 \text{ J/gmol } ^\circ\text{C})(100 - 21^\circ\text{C})(\text{kJ}/1000 \text{ J}) + 40.65 \text{ kJ/gmol}] = 11755 \text{ kJ/h} = 3.26 \text{ kJ/s}$$

A hairdryer supplies about 1500 W or 1.5 kJ/s. So one hairdryer is insufficient, but 3 could do the job.

P6.28

The Antoine equation for acetone at 1.5 atm (1140 mm Hg) is

$$\log_{10}(1140) = 7.02447 - \frac{1161.0}{T + 224}$$

Solving, $T = 68.6^\circ\text{C}$.

$\Delta\hat{H}_v$ is the difference in enthalpy between the liquid phase and the vapor phase. To calculate $\Delta\hat{H}_v$ at 68.6°C, we construct an enthalpy path as follows:

- (a) cool liquid at 1.5 atm from 68.6 °C to 56.5 °C
- (b) vaporize liquid at 56.5 °C
- (c) heat vapor from 56.5 °C to 68.6 °C

(We'll neglect any effects of pressure.) We look up heat capacity polynomials in Table B.17 and remember to convert from Celsius to Kelvin:

$$\Delta\hat{H}_v(68.6^\circ\text{C}) = \int_{341.75}^{329.65} (72.2 + 0.186T) dT + 29,100 + \int_{329.65}^{341.75} (6.301 + 0.2606T - 1.253 \times 10^{-4} T^2 + 2.038 \times 10^{-8} T^3) dT$$

$$\Delta\hat{H}_v(68.6^\circ\text{C}) = -1629 + 29100 + 973 = 28444 \text{ J/gmol}$$

The general equation is

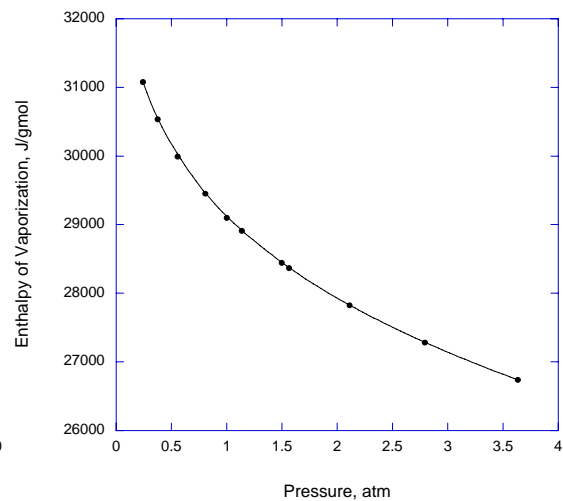
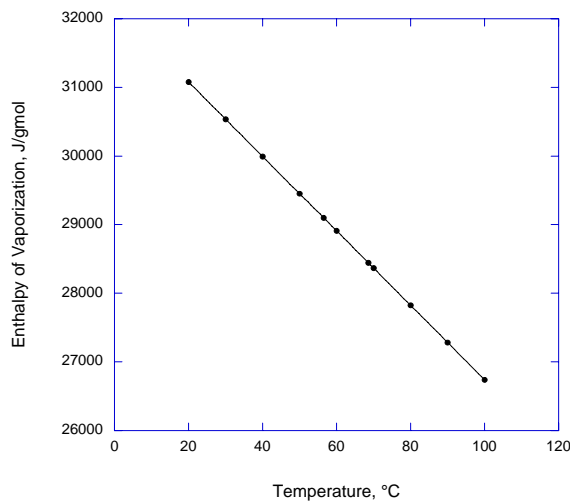
$$\Delta\hat{H}_v(T_B) = \int_{T_b}^{329.65} (72.2 + 0.186T) dT + 29,100 + \int_{329.65}^{T_B} (6.301 + 0.2606T - 1.253 \times 10^{-4} T^2 + 2.038 \times 10^{-8} T^3) dT$$

where T_b is the temperature of interest. T_b is related to P via the Antoine equation

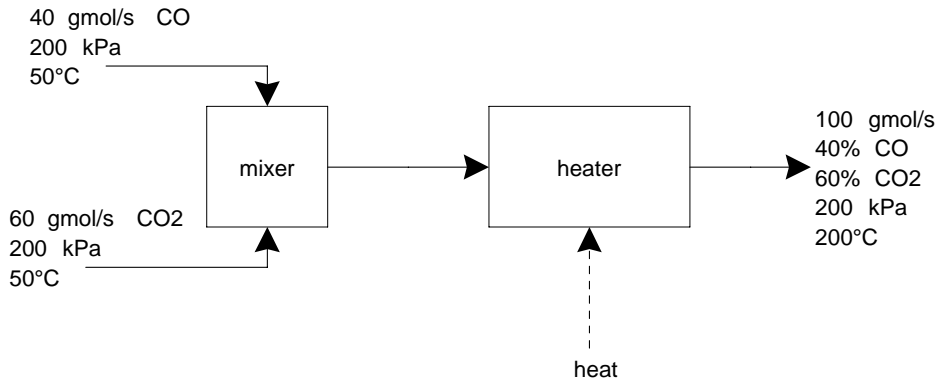
$$\log_{10} P = 7.02447 - \frac{1161.0}{T_b + 224}$$

Thus, given any pressure, we can calculate the boiling point temperature and the enthalpy of vaporization at that pressure. This strategy was used to calculate $\Delta\hat{H}_v$ over a range from 20 – 100 °C. The results are tabulated and plotted.

T °C	20	30	40	50	56.5	60	68.6	70	80	90	100
P atm	0.24	0.37	0.56	0.806	1.0	1.14	1.5	1.56	2.11	2.79	3.63
$\Delta\hat{H}_v$, kJ/gmol	31.1	30.4	30.0	29.5	29.1	28.9	28.4	28.4	27.8	27.3	26.7



The enthalpy of vaporization decreases linearly with temperature and exponentially with pressure.

P6.29

The entire process is the system. The material balance is solved (as shown on the flow diagram) assuming steady state operation. The energy balance equation is

$$\dot{n}_{out}\hat{H}_{out} - (\dot{n}_{CO,in}\hat{H}_{CO,in} + \dot{n}_{CO_2,in}\hat{H}_{CO_2,in}) = \dot{Q}$$

The flow rates in and out are known, and the conditions of the inlet and outlet streams (phase, temperature, pressure, composition) are all known, so their enthalpies can be determined. If we choose pure streams at 200 kPa and 50°C as the reference state, then $\hat{H}_{CO,in} = \hat{H}_{CO_2,in} = 0$. Now we need to determine \hat{H}_{out} based on this reference state. We construct an enthalpy path from the reference state to the outlet state by (a) heating the pure gas streams from 50°C to 200°C at 200 kPa and (b) mixing the two gas streams together at 200°C and 200 kPa.

(a) for CO

$$\Delta H = \dot{n}_{CO} \int_{T_{ref}}^{T_{out}} C_{p,CO} dT = 40 \times \int_{323}^{573} (30.87 - 0.01285T + 2.789 \times 10^{-5}T^2 - 1.272 \times 10^{-8}T^3) dT$$

$$\Delta H = 296,175 \text{ J/s}$$

for CO₂

$$\Delta H = \dot{n}_{CO_2} \int_{T_{ref}}^{T_{out}} C_{p,CO_2} dT = 60 \times \int_{323}^{573} (19.80 + 0.07344T - 5.602 \times 10^{-5}T^2 + 1.7115 \times 10^{-8}T^3) dT$$

$$\Delta H = 642,369 \text{ J/s}$$

(b) Since these are both gases, we assume enthalpy of mixing is zero.

Therefore

$$\dot{Q} = 296,175 + 642,369 = 938,544 \text{ J/s} = 938.5 \text{ kJ/s}$$

(If you use the approximate C_p , the answer is 507 kJ/s).

P6.30

From Table B.22, at 18°C

$$\Delta \hat{H}_{soln} = -23.3 \text{ kJ/gmol for Na}_2\text{CO}_3$$

$$\Delta \hat{H}_{soln} = -9.16 \text{ kJ/gmol for Na}_2\text{CO}_3 \bullet \text{H}_2\text{O}$$

$$\Delta \hat{H}_{soln} = +45.22 \text{ kJ/gmol for Na}_2\text{CO}_3 \bullet 7\text{H}_2\text{O}$$

$$\Delta \hat{H}_{soln} = +67.86 \text{ kJ/gmol for Na}_2\text{CO}_3 \bullet 10\text{H}_2\text{O}$$

With an insulated rigid container, there is no heat or work term. There is also no change in kinetic or potential energy, and no change in mass if we consider the initial system to be the powder and the water, and the final system to be the solution. The integral energy balance reduces to

$$U_{sys,f} - U_{sys,0} = 0$$

If we choose the pure components in their normal state of aggregation (i.e., solid for sodium carbonate and liquid for water) at 20°C and 1 atm as the reference state, then

$$U_{sys,0} = 0$$

To calculate the final internal energy we divide into 3 steps:

(a) change temperature of pure components from 20°C to 18°C

(b) dissolve powder and liquid at 18°C

(c) change temperature of solution from 18°C to T_f .

$\Delta \hat{H}_{soln} \cong \Delta \hat{U}_{soln}$ and for liquids and solids $C_p \cong C_v$, and we'll assume that the heat capacity of the dilute solution is the same as that of water. From the NIST Chemistry Webbook we find that $C_p = 110 \text{ J/gmol K} = 1.0 \text{ J/g K}$ for solid sodium carbonate. For water, $C_p = 75.4 \text{ J/gmol K} = 4.18 \text{ J/g K}$. 5 L of water equals 5000 g at a density of 1 g/mL. Let's work out the numbers for Na_2CO_3 first:

$$(a) \sum mC_v \Delta T = 5000 \times 4.18 \times (-2^\circ\text{C}) + 1 \times 1.0 \times (-2^\circ\text{C}) = 41,800 \text{ J}$$

$$(b) \Delta U_{soln} = (-23.3 \text{ kJ/gmol solute}) \times (1 \text{ g}/106 \text{ g/gmol}) \times (1000 \text{ J/kJ}) = -219.8 \text{ J}$$

$$(c) mC_v \Delta T = 5001 \times 4.18 \times (T_f - 18) = 20904(T_f - 18) \text{ J}$$

Returning to the energy balance equation

$$U_{sys,f} = 0 = 41800 - 219.8 + 20904(T_f - 18)$$

$$T_f = 19.989^\circ\text{C}$$

So the temperature has decreased by 0.011°C.

We complete similar calculations and summarize

Na_2CO_3 : Temperature decreases by 0.011°C

$\text{Na}_2\text{CO}_3 \bullet \text{H}_2\text{O}$: Temperature decreases by 0.0045°C

$\text{Na}_2\text{CO}_3 \bullet 7\text{H}_2\text{O}$: Temperature increases by 0.02°C

$\text{Na}_2\text{CO}_3 \bullet 10\text{H}_2\text{O}$: Temperature increases by 0.03°C

Your thermometer would have to be extraordinarily precise, and your insulation perfect, to use this method to identify the solids. However, you might have better luck if you relaxed the infinite dilution assumption and added, say, 10 or 50 or even 100 g of powder to the water. It is likely then you would at least be able to tell whether the sample is anhydrous or heavily hydrated.

P6.31

Ethanol: The combustion reaction is $\text{C}_2\text{H}_5\text{OH} + 3\text{O}_2 \rightarrow 2\text{CO}_2 + 3\text{H}_2\text{O}$. We'll base our calculation on liquid ethanol combusted and liquid water generated. From App. B, we find $\Delta\hat{H}_f$. Using the molar mass of 46 g/gmol, we get

$$\Delta\hat{H}_c = \frac{(-1)(-463.3) + 2(-393.5) + 3(-285.84)}{46} = -25.68 \text{ kJ/g ethanol}$$

CO_2 emissions is 2 gmol CO_2 /gmol ethanol, or 1.9 g CO_2 /g ethanol.

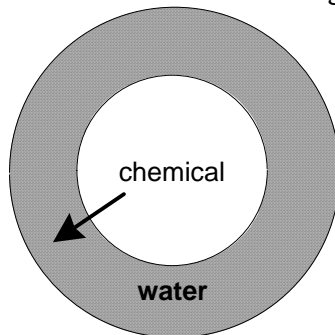
Hydrazine: $\text{N}_2\text{H}_4 + \text{O}_2 \rightarrow \text{N}_2 + 2\text{H}_2\text{O}$ A similar calculation gives

$$\Delta\hat{H}_c = \frac{(-1)(95.353) + 2(-285.84)}{38} = -20.85 \text{ kJ/g hydrazine}$$

with zero CO_2 emissions. Ethanol has a low energy density compared to gasoline, which is a concern some people have regarding its use as a transportation fuel. Hydrazine has a surprisingly low energy density, given that it is used as a rocket fuel. However it has some advantages as a rocket fuel (and disadvantages as a fuel for every day). It is highly unstable, and does not require an external ignition source. In rockets, hydrazine is commonly not oxidized but is decomposed rapidly to large quantities of hot N_2 and H_2 ; it has a high specific impulse (thrust produced per kg of product decomposed in one second).

P6.32

In the inner chamber, the chemical is combusted. Heat, as indicated by the arrow, travels between the inner and outer chamber. No mass is exchanged between the two chambers.



First, let's consider the water as the system. We use an integral energy balance equation, with no mass entering or leaving the system, no change in kinetic or potential energy, and no work:

$$U_{sys,f} - U_{sys,0} = Q$$

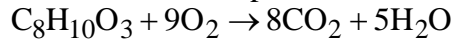
The change in energy is at constant volume and is due to a change in temperature. For water, $C_p = C_v = 4.18 \text{ J/g } ^\circ\text{C}$, and

$$U_{sys,f} - U_{sys,0} = Q = mC_v(T_f - T_0) = 650 \times 4.18 \times (36.2 - 23.6) = 34234 \text{ J}$$

Now we consider the inner chamber as the system. We have

$$U_{sys,f} - U_{sys,0} = Q = -34234 \text{ J}$$

A chemical reaction takes place in the inner chamber:



As a reasonable approximation, we assume that virtually all of the change in energy of this system is due to the reaction (we neglect the small increase in temperature).

Therefore

$$U_{sys,f} - U_{sys,0} = n_r \Delta \hat{U}_r = -34234 \text{ J}$$

where n_r is the moles of reaction, which is $2.7 \text{ g}/154 \text{ g/gmol}$ or 0.0175 gmol . Therefore,

$$\Delta \hat{U}_r = -\frac{34234 \text{ J}}{0.0175 \text{ gmol}} = -1956 \text{ kJ/gmol}$$

There is a change in moles in the gas phase, if we assume the chemical and water are in the liquid phase then this change is $(9 - 8)$ or -1 mole, therefore

$$\Delta \hat{H}_r = \Delta \hat{U}_r + RT \Delta n_R = -1956 + (0.0083144 \times 298 \times (-1)) = -1958 \text{ kJ/gmol}$$

Now we know that

$$\Delta \hat{H}_r = \sum \nu_i \Delta \hat{H}_{f,i} = (-1) \Delta \hat{H}_{f,\text{C}_8\text{H}_{10}\text{O}_3} + (-9)(0) + 8(-393.5) + 5(-285.84) = -1958 \text{ kJ/gmol}$$

or

$$\Delta \hat{H}_{f,\text{C}_8\text{H}_{10}\text{O}_3} = -2620 \text{ kJ/gmol}$$

P6.33

We'll assume that there is no heat loss from the cold pack during the rapid mixing of the ammonium nitrate with the water. Then the energy balance over this short period of time is simply

$$U_{sys,f} - U_{sys,0} = 0$$

We consider two steps: (1) mixing and dissolution of ammonium nitrate and water at 22°C and 1 atm and (2) decreasing of solution temperature from 22 °C to final temperature. For the step (1):

$$\Delta U_{\text{soln}} \cong \Delta H_{\text{soln}} = \frac{6.47 \text{ kcal}}{\text{gmol}} \times \frac{1000 \text{ cal}}{\text{kcal}} \times \frac{\text{gmol}}{80 \text{ g}} \times 25 \text{ g} = 2021 \text{ cal}$$

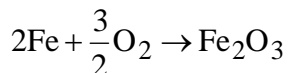
For step (2), assuming the heat capacity of the solution is the same as that of water:

$$\Delta U = mC_v(T_f - 22) = 275 \text{ g} \times \frac{1 \text{ cal}}{\text{g } ^\circ\text{C}} \times (T_f - 22)$$

Combining, $U_{\text{sys},f} - U_{\text{sys},0} = 0 = 2021 + 275(T_f - 22)$
 $T_f = 14.6^\circ\text{C}$ (about 58°F)

P6.34

The reaction is



which is just the formation reaction for Fe₂O₃, for which

$$\Delta \hat{H}_f = -830.5 \text{ kJ/gmol}$$

The total heat release desired is 600 kJ. (How would you design the hot pack to control the rate of heat release??) Therefore we need to generate (-600/-830.5) or 0.722 gmol Fe₂O₃, which requires that 1.44 gmol Fe react. Since the molar mass of Fe is 56 g/gmol, we should put (1.44)(56) or about 80 g Fe filings in the hot pack.

Oxygen is supplied by diffusion into the hotpack from the air. The final mass is 0.722 gmol x 160 g/gmol or 115 g Fe₂O₃. The mass increases about 35 g, or by about 44%.

P6.35

(a) Tank is system. For first steam (assuming well-mixed), need to heat all water just up to 99.6°C (saturated water at 1 bar).

$$U_{\text{sys},f} - U_{\text{sys},0} = 25 \text{ kg}(75.4 \text{ J/gmol } ^\circ\text{C})(1 \text{ gmol}/18 \text{ g})(99.6^\circ\text{C} - 20^\circ\text{C})(1 \text{ kJ}/1000 \text{ J}) = 8336 \text{ kJ}$$

$$8336 = (15 \text{ kJ/s})t,$$

$$\text{or } t = 555 \text{ s}$$

(b) To vaporize all saturated water to saturated steam, use steam tables

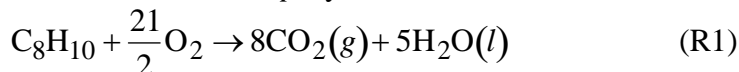
$$25 \text{ kg}(2674.9 - 417.50 \text{ kJ/kg}) = 56,435 \text{ kJ}$$

$$56,435 \text{ kJ} = 15t$$

$$\text{or } t = 3760 \text{ s}$$

P6.36

The combustion reaction for *p*-xylene is

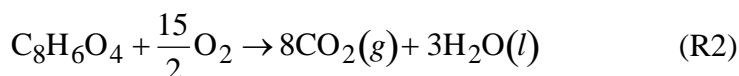


for which we have $\Delta\hat{H}_{c,px}^\circ = -1089$ kcal/gmol, with

$$\Delta\hat{H}_{c,px}^\circ = -1089 = \sum_i \nu_{i1} \Delta\hat{H}_{f,i}^\circ = (-1)\Delta\hat{H}_{f,px}^\circ + 8(-94) + 5(-68)$$

$$\Delta\hat{H}_{f,px}^\circ = -3 \text{ kcal/gmol}$$

The combustion reaction for TPA is



for which we have $\Delta\hat{H}_{c,TPA}^\circ = -770$ kcal/gmol, with

$$\Delta\hat{H}_{c,TPA}^\circ = -770 = \sum_i \nu_{i1} \Delta\hat{H}_{f,i}^\circ = (-1)\Delta\hat{H}_{f,TPA}^\circ + 8(-94) + 3(-68)$$

$$\Delta\hat{H}_{f,TPA}^\circ = -186 \text{ kcal/gmol}$$

For the reaction of interest (which is simply (R1) – (R2)!) we calculate

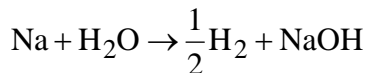
$$\Delta\hat{H}_r^\circ = \sum_i \nu_{i1} \Delta\hat{H}_{f,i}^\circ = (-1)(-3) + 1(-186) + 2(-68)$$

$$\Delta\hat{H}_r^\circ = -319 \text{ kcal/gmol}$$

(or, we can subtract the enthalpy of combustion of TPA from that of *p*-xylene to get the same answer.)

P6.37

The reaction is



$$\Delta\hat{H}_r^\circ = \sum_i \nu_{i1} \Delta\hat{H}_{f,i}^\circ = (-1)(-285.84) + 1(-425.9) = -140 \text{ kJ/gmol}.$$

1 mL water = 1 g water = 0.056 gmol. 100 g Na = 4.35 gmoles. If all water reacts, about 4.35 – 0.056 = 4.29 gmol or about 98.7 g of Na remain. The heat capacity of Na is 28 J/gmol °C (Lange's Handbook of Chemistry). The energy balance (assuming no heat and no work) is

$$(-140 \text{ kJ/gmol reaction}) \times (0.056 \text{ gmol}) + (4.29 \text{ gmol}) \times (28 \text{ J.gmol } ^\circ\text{C}) \times (\Delta T) = 0$$

$$\Delta T = 65^\circ\text{C}$$

The heat released upon reaction is sufficient to warm the Na metal up by about 65°C, or, to about 85 - 90°C from room temperature. This may be enough to cause the hydrogen gas to explode.

If a small amount of sodium metal added to a large quantity of water, the high heat capacity of the water tends to “absorb” the heat of reaction – the water temperature will rise, but the hydrogen gas won’t ignite.

P6.38

From Lange’s Handbook of Chemistry (15th edition) we find

$$\Delta \hat{H}_{f,\text{glucose}}^{\circ} = -1273.3 \text{ kJ/gmol}$$

$$\Delta \hat{G}_{f,\text{glucose}}^{\circ} = -910.4 \text{ kJ/gmol}$$

Assuming liquid water as the product,

$$\Delta \hat{H}_r^{\circ} = \sum_i \nu_{i1} \Delta \hat{H}_{f,i}^{\circ} = (-1)(-1273.3) + (6)(-393.5) + (6)(-285.84) = -2802.7 \text{ kJ/gmol}$$

$$\Delta \hat{G}_r^{\circ} = \sum_i \nu_{i1} \Delta \hat{G}_{f,i}^{\circ} = (-1)(-910.4) + (6)(-394.37) + (6)(-237.19) = -2879 \text{ kJ/gmol}$$

$$\text{For, ADP to ATP conversion, } \Delta \hat{G}_r^{\circ} = + \frac{7.3 \text{ kcal}}{\text{gmol}} \times \frac{4.184 \text{ kJ}}{\text{kcal}} = +30.54 \text{ kJ/gmol}$$

There are 6 moles of ADP converted to ATP per mole of oxygen consumed by aerobic metabolism of glucose, and there are 6 moles oxygen consumed per mole glucose consumed, so there are 36 moles ADP converted to ATP per mole glucose consumed.

The efficiency of conversion is

$$\frac{36 \times 30.54}{2879} \times 100\% = 38\%$$

5 g of glucose = 0.0278 gmol glucose. The enthalpy change associated with complete oxidation of this much glucose is (0.0278 gmol)(-2802.7 kJ/gmol consumed) or -77.9 kJ. Assuming no heat or work terms, the system energy does not change, and the internal energy change associated with reaction must be exactly compensated by a change in temperature of the water (assuming no phase change). Estimating $C_v = C_p = 4 \text{ J/g } ^{\circ}\text{C}$, and a density of 1 g/mL for water, and assuming that the water starts at warm room temperature:

$$(-77.9 \text{ kJ})(1000 \text{ J/kJ}) + (100 \text{ g})(4 \text{ J/g}^{\circ}\text{C})(T_f - 25^{\circ}\text{C}) = 0$$

$$T_f \approx 195^{\circ}\text{C}!!$$

Wow! Our assumption of no phase change is clearly incorrect. Let’s assume that at least some of the water evaporates, and use an approximate measure of 2000 J/g for the enthalpy of vaporization:

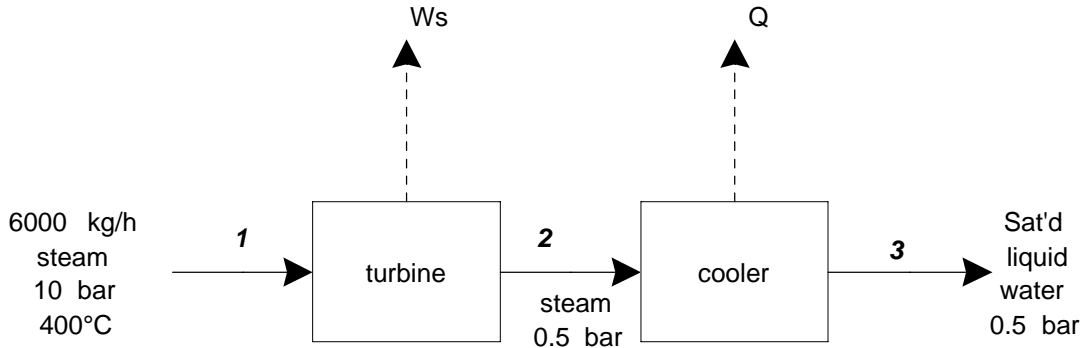
$$(-77.9 \text{ kJ})(1000 \text{ J/kJ}) + (100 \text{ g})(4 \text{ J/g}^\circ\text{C})(100^\circ\text{C} - 25^\circ\text{C}) + m_{\text{evap}}(2000 \text{ J/g}) = 0$$

$$m_{\text{evap}} \approx 24 \text{ g}$$

Glucose oxidation releases enough energy to vaporize about 1/4 of the water in the beaker!

P6.39

Steps 1 and 2. Draw a diagram and define system.



Since we need to solve for stream 2, we need to choose a system that includes stream 2 crossing its boundary. We will use two systems: the turbine, and the cooler, in different parts of the problem.

Steps 3-5. Choose components, define stream variables, check units, define basis.

Units are consistent, the component is water W , the basis is 6000 kg/h steam in stream 1.

Step 6. Set up and solve process flows.

This is simple! (We assume steady state.) $\dot{m}_1 = \dot{m}_2 = \dot{m}_3 = 6000 \text{ kg/h}$

Step 7. Define energy of process streams

Kinetic energy and potential energy differences between the inlet and outlet streams are negligible. The temperature and pressure of the steam entering the turbine (stream 1) is known. From a steam table, we find

$$\hat{H}_1 = 3264.5 \text{ kJ/kg}$$

The pressure of stream 3 is known, and furthermore we know that it is saturated liquid, so its condition is fully specified. From the NIST Chemistry Webbook I find that at 0.5 bar and saturation,

$$\hat{H}_3 = 340.54 \text{ kJ/kg}$$

Step 8. Identify heat and work.

The heat flow is known, it is out of the cooler so the term is negative:

$$\dot{Q} = -1.25 \times 10^7 \text{ kJ/h}$$

There is a work term associated with the turbine, \dot{W}_s , that is not yet known.

Step 9. Define changes in system energy

Since the system is at steady state, there is no change in system energy.

Steps 10-12: Write energy balance, solve, check.

The differential steady-state energy balance equation, with the turbine as the system, is

$$\dot{m}_1 \hat{H}_1 - \dot{m}_2 \hat{H}_2 + \dot{W}_s = 0 = (6000)(3264.5) - (6000)\hat{H}_2 + \dot{W}_s$$

With the cooler as the system, the energy balance equation is

$$\dot{m}_2 \hat{H}_2 - \dot{m}_3 \hat{H}_3 + \dot{Q} = 0 = (6000)\hat{H}_2 - (6000)(340.54) - 1.25 \times 10^7 = 0$$

Solving the second equation first,

$$\hat{H}_2 = 2424 \text{ kJ/kg}$$

At 0.5 bar and saturation temperature, from the NIST Chemistry Webbook,

$\hat{H}_{\text{steam}} = 2645.2 \text{ kJ/kg}$ and $\hat{H}_{\text{liquid}} = 340.54 \text{ kJ/kg}$. The enthalpy of stream 2 is in between these two values, so the stream must be a mix of vapor and liquid:

$$\dot{m}_2 \hat{H}_2 = 2424 \text{ kJ/kg} = \dot{m}_{\text{steam}} \hat{H}_{\text{steam}} + \dot{m}_{\text{liquid}} \hat{H}_{\text{liquid}} = \dot{m}_{\text{steam}} (2645.2) + \dot{m}_{\text{liquid}} (340.54)$$

Also

$$\dot{m}_{\text{steam}} + \dot{m}_{\text{liquid}} = \dot{m}_2 = 6000$$

Simultaneous solution yields

$$\dot{m}_{\text{steam}} = 5424 \text{ kg/h and stream 2 is } (5424/6000) \times 100 \text{ or } 90\% \text{ vapor.}$$

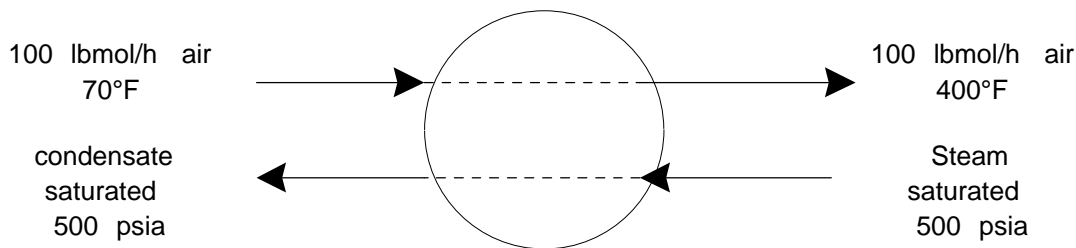
Finally, returning to the energy balance around the turbine

$$(6000)(3264.5) - (6000)(2424) = -\dot{W}_s$$

$$\dot{W}_s = -5.04 \times 10^6 \text{ kJ/h} = -1400 \text{ kW}$$

P6.40

Steps 1 and 2. Draw a diagram and define system.



We've sketched a heat exchanger. The dashed lines indicate the material flows through the exchangers but the streams do not mix. We choose the exchanger and its contents as the system, operated at steady state.

Steps 3-5. Choose components, define stream variables, check units, define basis.
Components are air A and steam/water W. Streams will be defined as “in” or “out”.

Step 6. Set up and solve process flows.

$$\dot{N}_{A,in} = \dot{N}_{A,out} = 100 \text{ lbmol/h} \text{ and } \dot{N}_{W,in} = \dot{N}_{W,out} = \dot{N}_W$$

Step 7. Define energy of process streams

We can choose air at 70°F and operating pressure as the reference state for the air. We neglect kinetic and potential energy changes. The only change in the enthalpy of the air stream is due to the change in temperature. Therefore;

$$\hat{H}_{A,in} = 0, \text{ and}$$

$$\hat{H}_{A,out} = \int_{T_{ref}}^{T_{out}} C_{p,A} dT = (7 \text{ Btu/lbmol } ^\circ\text{F})(400 - 70^\circ\text{F}) = 2310 \text{ Btu/lbmol}$$

We find the enthalpy of saturated steam and condensate from the NIST steam tables:

$$\hat{H}_{W,in} = 1205.8 \text{ Btu/lb} \text{ (saturated steam at 500 psia)}$$

$$\hat{H}_{W,out} = 449.8 \text{ Btu/lb} \text{ (saturated liquid at 500 psia)}$$

Step 8. Identify heat and work.

None; we assume the heat exchanger is insulated so there is no heat transferred to/from the outside to the system.

Step 9. Define changes in system energy

None – we assume steady state operation.

Steps 10-12: Write energy balance, solve, check.

The steady-state differential energy balance equation is

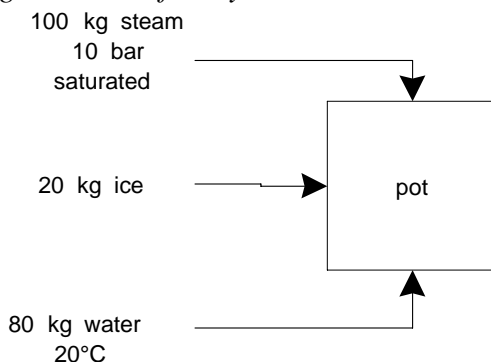
$$(\dot{N}_{A,in} \hat{H}_{A,in} + \dot{N}_{W,in} \hat{H}_{W,in}) - (\dot{N}_{A,out} \hat{H}_{A,out} + \dot{N}_{W,out} \hat{H}_{W,out}) = 0$$

$$(0 + \dot{N}_W \times 1205.8 \text{ Btu/lb} \times 18 \text{ lb/lbmol}) = (100 \text{ lbmol/h} \times 2310 \text{ Btu/lbmol} + \dot{N}_W \times 449.8 \text{ Btu/lb} \times 18 \text{ lb/lbmol})$$

$$\dot{N}_W = 17 \text{ lbmol/h} = 305 \text{ lb/h}$$

P6.41

Steps 1 and 2. Draw a diagram and define system.



The system is the pot and its contents.

Steps 3-5. Choose components, define stream variables, check units, define basis.

H₂O is the only component. We'll identify the streams as steam, ice and liquid. The system mass and energy both change from the initial to the final state.

Step 6. Set up and solve process flows.

An integral material balance, assuming the pot is initially empty, tells us

$$m_{sys,f} = 100 + 20 + 80 = 200 \text{ kg}$$

Step 7. Define energy of process streams

We have many choices for the reference state. Let's pick ice (presumably at 0°C) as the reference state. We'll use the following data:

$\Delta \hat{H}_m = 6.008 \text{ kJ/gmol} = 333.8 \text{ kJ/kg}$ (Table B.20, assumed independent of pressure)

$$C_{p, \text{liquid}} = 75.4 \text{ J/gmol } ^\circ\text{C} = 4.18 \text{ kJ/kg } ^\circ\text{C}$$

$$\Delta \hat{H}_v = 2777.1 - 762.52 = 2014.6 \text{ kJ/kg at 10 bar (179.88}^\circ\text{C, Table B.16)}$$

Now we calculate the enthalpy of each incoming stream:

$$\hat{H}_{ice} = 0$$

$$\hat{H}_{liquid} = 333.8 \text{ kJ/kg} + 4.18 \text{ kJ/kg } ^\circ\text{C} \times (20 - 0^\circ\text{C}) = 417.4 \text{ kJ/kg}$$

$$\hat{H}_{steam} = 333.8 \text{ kJ/kg} + 4.18 \text{ kJ/kg } ^\circ\text{C} \times (179.88 - 0^\circ\text{C}) + 2014.6 = 3100.3 \text{ kJ/kg}$$

Kinetic and potential energy terms are assumed negligible.

Step 8. Identify heat and work.

There are no heat or work terms.

Step 9. Define changes in system energy

The system energy U_{sys} must be defined on the same reference state as the energy of the process streams (0°C, ice, 10 bar). We will use

$$\Delta \hat{U}_m \cong \Delta \hat{H}_m = 333.8 \text{ kJ/kg}$$

$$C_{v, \text{liquid}} = C_{p, \text{liquid}} = 4.18 \text{ kJ/kg } ^\circ\text{C}$$

$$\Delta \hat{U}_v = 2582.7 - 761.39 = 1821.3 \text{ kJ/kg}$$

to relate system internal energy to T , P and phase.

Steps 10-12: Write energy balance, solve, check.

The integral energy balance equation simplifies to:

$$U_{sys,f} = H_{in}$$

$$m_{sys,f} \hat{U}_{sys,f} = m_{ice} \hat{H}_{ice} + m_{liquid} \hat{H}_{liquid} + m_{steam} \hat{H}_{steam}$$

$$(200 \text{ kg}) \hat{U}_{sys,f} = 0 + (80 \text{ kg})(417.4 \text{ kJ/kg}) + (100 \text{ kg})(3100.3 \text{ kJ/kg})$$

$$\hat{U}_{sys,f} = 1717.1 \text{ kJ/kg}$$

Comparing to the data in Step 9, the final mixture is a mix of liquid and steam.

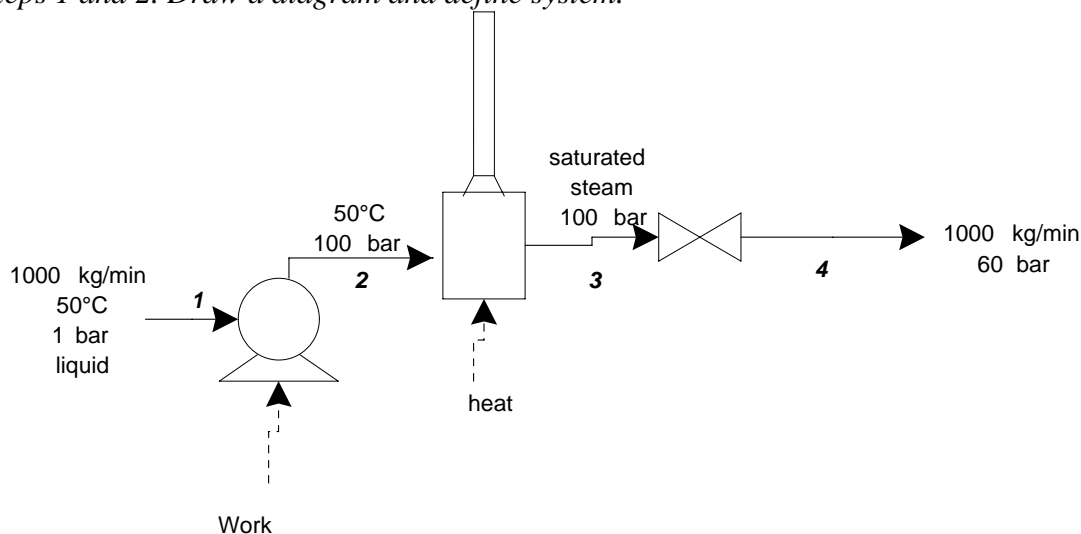
$$\hat{U}_{sys,f} = 1717.1 \text{ kJ/kg} = 333.8 + 4.18(179.88 - 0) + f_v(1821.3)$$

$$f_v = 0.35$$

where f_v = fraction vaporized. Since both vapor and liquid are present and at equilibrium, then we must be at saturation temperature. The final mixture is 35% vapor, 65% liquid, at 10 bar and 179.88°C.

P6.42

Steps 1 and 2. Draw a diagram and define system.



We will use the contents of the pump, the furnace, and the expansion valve as the systems.

Steps 3-5. Choose components, define stream variables, check units, define basis.

The component is H_2O . Streams are numbered. Basis is 1000 kg/min. Energy units are kJ.

Step 6. Set up and solve process flows.

$$\dot{m}_1 = \dot{m}_2 = \dot{m}_3 = \dot{m}_4 = 1000 \text{ kg/min}$$

Step 7. Define energy of process streams

We will worry only about enthalpy and neglect kinetic and potential energy. We use the steam tables as well as the stated conditions of T , P and phase:

$$\hat{H}_1 = 209.46 \text{ kJ/kg (liquid at } 50^\circ\text{C and 1 bar)}$$

$$\hat{H}_2 = 217.94 \text{ kJ/kg (liquid at } 50^\circ\text{C and } 100 \text{ bar)}$$

$$\hat{H}_3 = 2725.5 \text{ kJ/kg (saturated steam at } 100 \text{ bar, at which } T = 311^\circ\text{C)}$$

We don't know the temperature or phase of stream 4. Let's just collect some useful data at 60 bar:

$$\hat{H} = 1213.9 \text{ kJ/kg (saturated liquid at } 60 \text{ bar, at which } T = 275.58^\circ\text{C)}$$

$$\hat{H} = 2784.6 \text{ kJ/kg (saturated steam at } 60 \text{ bar, at which } T = 275.58^\circ\text{C)}$$

Step 8. Identify heat and work.

There is work input at the pump and heat input at the furnace. We do not yet know the numerical values of these energy flows.

Step 9. Define changes in system energy

At steady state, there is no change in system energy.

Steps 10-12: Write energy balance, solve, check.

Use steady-state differential energy balance equations. Start with the pump :

$$\dot{m}_2 \hat{H}_2 - \dot{m}_1 \hat{H}_1 = \dot{W}_s = 1000(217.94 - 209.46) = 8480 \text{ kJ/min}$$

The work term is positive, and the pump must supply 8480 kJ/min (189.5 hp – a large pump).

Then consider the furnace:

$$\dot{m}_3 \hat{H}_3 - \dot{m}_2 \hat{H}_2 = \dot{Q} = 1000(2725.5 - 217.94) = 2.51 \times 10^6 \text{ kJ/min}$$

The furnace must supply 12.51 million kJ/min, a significantly larger energy flow than that supplied by the pump.

Finally, consider the expansion valve:

$$\dot{m}_4 \hat{H}_4 - \dot{m}_3 \hat{H}_3 = 0 = 1000(\hat{H}_4 - 2725.5)$$

$$\hat{H}_4 = 2725.5 \text{ kJ/kg}$$

The enthalpy of the stream does not change across the expansion valve. However, the phase and temperature do change because the pressure has changed. The enthalpy is between that for saturated liquid and saturated vapor at 60 bar and therefore the stream must be a mix of liquid and vapor.

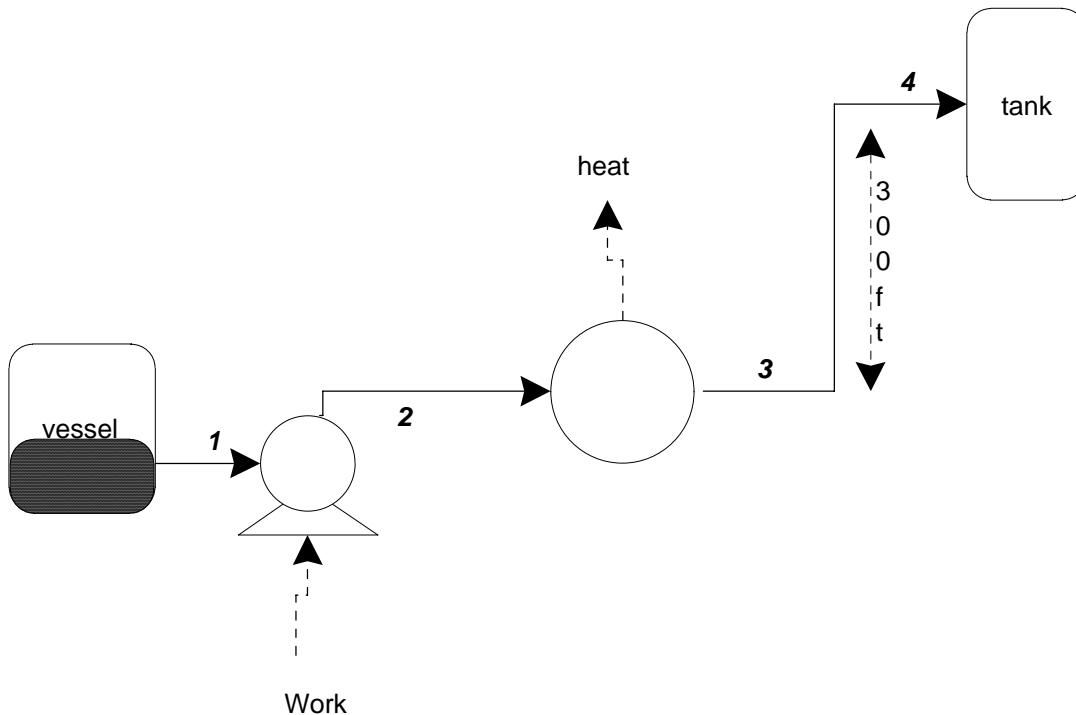
$$\hat{H}_4 = 2725.5 \text{ kJ/kg} = f_v(2784.6) + (1 - f_v)(1213.9)$$

$$f_v = 0.96$$

The stream exiting the expansion valve is 96% vapor, 4% liquid, 60 bar, and 275.58°C.

P6.43

Steps 1 and 2. Draw a diagram and define system.



We'll define our system as everything contained between the vessel and the tank on the hill.

Steps 3-5. Choose components, define stream variables, check units, define basis.

Oil is the component, and streams are numbered. The basis is 1400 gal/min; this needs to be converted to a mass flow rate:

$$\dot{m}_1 = \frac{1400 \text{ gal}}{\text{min}} \times \frac{\text{ft}^3}{7.4805 \text{ gal}} \times \frac{50 \text{ lb}}{\text{ft}^3} = \frac{9358 \text{ lb}}{\text{min}}$$

We will use Btu for energy units.

Step 6. Set up and solve process flows.

$$\dot{m}_1 = \dot{m}_2 = \dot{m}_3 = \dot{m}_4 = \frac{9358 \text{ lb}}{\text{min}}$$

Step 7. Define energy of process streams

We'll choose the oil at 80°F and at the elevation of the vessel as the reference state. We need to consider both enthalpy and potential energy; the fluid is quiescent in the vessel and in the tank so velocity = 0 at both the inlet and the outlet. The oil changes temperature between inlet and outlet but not phase or pressure. The oil at the inlet is at the same elevation but a different temperature than the reference state:

$$\hat{H}_1 = C_p (T_1 - T_{ref}) = 0.63 \text{ Btu/lb } ^\circ\text{F} (200 - 80^\circ\text{F}) = 75.6 \text{ Btu/lb}$$

$$\hat{E}_{p1} = 0$$

At the outlet the oil is at the same temperature as the reference state but a different elevation:

$$\hat{H}_4 = 0$$

$$\hat{E}_{p,4} = g(h_3 - h_{ref}) = 32.174 \text{ ft/s}^2 (300 \text{ ft}) \times \frac{\text{lb}_f}{32.174 \text{ lb ft/s}^2} \times \frac{\text{Btu}}{778.16 \text{ ft lb}_f} = 0.386 \text{ Btu/lb}$$

Step 8. Identify heat and work.

There is a work input at the pump and a heat output at the exchanger.

Step 9. Define changes in system energy

We assume steady-state operation, so there is no change in system energy.

Steps 10-12: Write energy balance, solve, check.

The overall energy balance simplifies to:

$$\dot{m}_4 (\hat{H}_4 + \hat{E}_{p,4}) - \dot{m}_1 (\hat{H}_1 + \hat{E}_{p,1}) = \dot{Q} + \dot{W}_s = 9358 \text{ lb/min} \times (0.386 - 75.6) = -703,850 \text{ Btu/min}$$

This isn't useful yet because we can't solve for heat or work flows independently. We recognize that the change in elevation is achieved through work and the change in temperature is achieved through heat exchange. Then we can associate heat flows with changes in enthalpy and work flows with changes in elevation. (See the Bernoulli equation.)

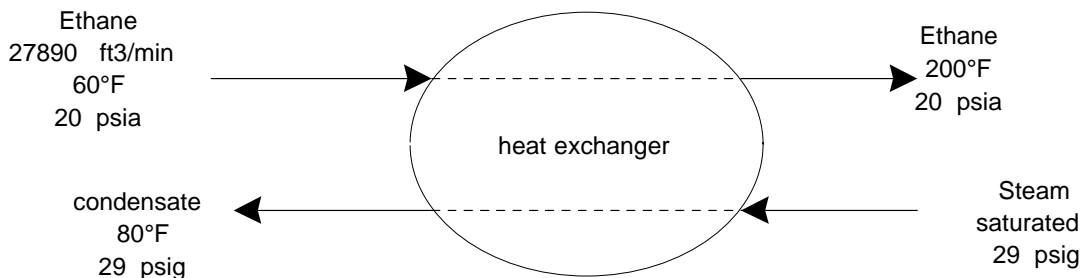
$$\dot{m}_4 \hat{H}_4 - \dot{m}_1 \hat{H}_1 = \dot{Q} = 9358 \text{ lb/min} \times (0 - 75.6) = -707,000 \text{ Btu/min}$$

$$\dot{m}_4 \hat{E}_{p,4} - \dot{m}_1 \hat{E}_{p,1} = \dot{W}_s = 9358 \text{ lb/min} \times (0.386 - 0) = +3612 \text{ Btu/min}$$

or, since 3412 Btu/h = 1.3405 hp, the work input from the pump is about 85 hp.

P6.44

Steps 1 and 2. Draw a diagram and define system.



The system is the contents of the heat exchanger.

Steps 3-5. Choose components, define stream variables, check units, define basis.

The components are ethane (E) and H₂O (W). The specified ethane flow rate is volumetric at the inlet conditions; we need to convert to a molar flow rate, which we do by using the ideal gas law:

$$\dot{n}_{E,in} = \frac{(20 \text{ psia})(27890 \text{ ft}^3/\text{min})}{(10.73 \text{ ft}^3\text{psia/lbmol } ^\circ\text{R})(60 + 459^\circ\text{R})} = 100 \text{ lbmol/min}$$

which serves as the basis.

Step 6. Set up and solve process flows.

$$\dot{n}_{E,in} = \dot{n}_{E,out} = 100 \text{ lbmol/min}$$

$$\dot{n}_{W,in} = \dot{n}_{W,out}$$

Step 7. Define energy of process streams

Enthalpy is the only energy form we need to consider, because changes in velocity and elevation are negligible.

For ethane, we'll choose the inlet conditions as the reference state: 20 psia and 60°F. The outlet stream differs from the reference state only with respect to temperature; the phase, pressure and composition stay the same. Therefore

$$\hat{H}_{E,in} = 0$$

$$\hat{H}_{E,out} = \int_{T_{ref}}^{T_{out}} C_{p,E} dT$$

Because the available heat capacity polynomial (Table B.17) is expressed in units of kJ, gmol, and °C, we will need to convert units. First, $T_{ref} = 60^\circ\text{F} = 15.6^\circ\text{C} = 288.7 \text{ K}$, and $T_{out} = 200^\circ\text{F} = 93.3^\circ\text{C} = 366.5 \text{ K}$. Then

$$\hat{H}_{E,out} = \int_{288.7}^{366.5} (5.409 + 0.2141T - 8.39 \times 10^{-5}T^2 + 1.373 \times 10^{-9}T^3) dT =$$

$$\hat{H}_{E,out} = 5178 \text{ J/gmol} \times 454 \text{ gmol/lbmol} \times 9.47817 \times 10^{-4} \text{ Btu/J} = 2228 \text{ Btu/lbmol}$$

For steam and water, we can either use the steam tables given in the text, (interpolating and converting units as needed), or go to the NIST Chemistry Webbook. At 80°F and 29 psig (43.7 psia), we find

$$\hat{H}_{W,out} = 868.6 \text{ Btu/lbmol}$$

For saturated steam at 43.7 psia (272.6°F)

$$\hat{H}_{W,in} = 21120 \text{ Btu/lbmol}$$

Also, of use later in this problem, we find from the same source that the specific volume of the saturated steam is 174.1 ft³/lbmol.

Step 8. Identify heat and work.

There are no heat or work terms, as the heat exchanger is assumed to be well insulated and there is no mechanical equipment.

Step 9. Define changes in system energy

No changes, the system is at steady state.

Steps 10-12: Write energy balance, solve, check.

The differential energy balance equation simplifies to

$$\dot{n}_{E,in} \hat{H}_{E,in} + \dot{n}_{W,in} \hat{H}_{W,in} - \dot{n}_{E,out} \hat{H}_{E,out} + \dot{n}_{W,out} \hat{H}_{W,out} = 0$$

or, using the material balance and rearranging:

$$\dot{n}_{E,in} (\hat{H}_{E,out} - \hat{H}_{E,in}) = \dot{n}_{W,in} (\hat{H}_{W,in} - \hat{H}_{W,out})$$

$$100(2228 - 0) = \dot{n}_{W,in} (21120 - 868.6)$$

$$\dot{n}_{W,in} = 11 \text{ lbmol/min}$$

Now, using that specific molar volume of steam at the inlet conditions we find the volumetric flow rate:

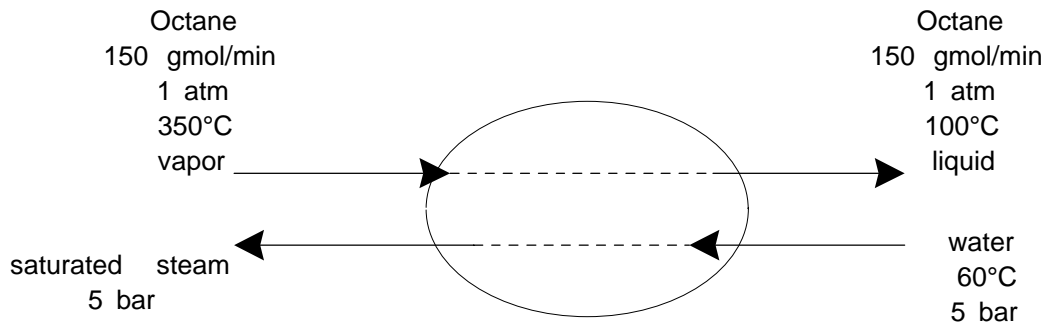
$$11 \text{ lbmol/min} \times 174.1 \text{ ft}^3/\text{lbmol} = 1915 \text{ ft}^3/\text{min}$$

To calculate the rate of heat to the ethane, we change the system to include only the ethane stream, in which case there is a heat input term. The energy balance is

$$\dot{Q} = \dot{n}_{E,in} (\hat{H}_{E,out} - \hat{H}_{E,in}) = 100(2228 - 0) = 222,800 \text{ Btu/min}$$

P6.45

Steps 1 and 2. Draw a diagram and define system.



The system is the contents of the heat exchanger. The dashed lines indicate that the stream flows do not mix inside the system.

Steps 3-5. Choose components, define stream variables, check units, define basis.

Components are octane (O) and H₂O (W). Streams are indicated as In or Out. The basis is $\dot{m}_{O,In} = 150$ gmol/min. Since the answer is desired in kg/min, it may be better to switch to mass units. The molar mass of octane is 114 g/gmol, so

$$m_{O,In} = 150 \times 114 = 17,100 \text{ g/min} = 17.1 \text{ kg/min}$$

Step 6. Set up and solve process flows.

$$\dot{m}_{O,In} = \dot{m}_{O,Out} = 17.1 \text{ kg/min}$$

$$\dot{m}_{W,In} = \dot{m}_{W,Out}$$

Step 7. Define energy of process streams.

By the rules of thumb, $C_p \sim 2$ J/g °C for organic liquids, $C_p \sim 1$ J/g °C for gases, and $\Delta\hat{H}_v \approx 500$ kJ/kg for organic compounds, and $C_p \sim 4$ J/g °C for water, $C_p \sim 1$ J/g °C for steam, and $\Delta\hat{H}_v \approx 2000$ kJ/kg for water. The boiling point temperature of n-octane is 125.7°C at 1 atm, and that for water is 151.8°C at 5 bar.

If we choose liquid at 100°C and 1 atm as the reference state for n-octane, then by the rules of thumb

$$\hat{H}_{O,out} = 0$$

$$\hat{H}_{O,in} \approx 2(125.7 - 100) + 500 + 1(350 - 125.7) = 775 \text{ J/g}$$

If we choose liquid at 60°C and 5 bar as reference state for water, then

$$\hat{H}_{W,in} = 0$$

$$\hat{H}_{W,out} \approx 4(151.8 - 60) + 2000 = 2367 \text{ J/g}$$

(We will go back and complete accurate calculations later.)

Step 8. Identify heat and work.

The heat exchanger is assumed to be well-insulated, so there is no heat term. With no mechanical equipment, there is no work term.

Step 9. Define changes in system energy

The system is assumed to be at steady state, so no changes in system energy.

Steps 10-12: Write energy balance, solve, check.

With substitution and re-arrangement, the differential energy balance equation simplifies to:

$$\dot{m}_{O,in} (\hat{H}_{O,in} - \hat{H}_{O,out}) = \dot{m}_{W,in} (\hat{H}_{W,out} + \hat{H}_{W,in})$$

$$\dot{m}_{W,in} = 17.1 \text{ kg/min} \frac{(775 \text{ kJ/kg})}{(2367 \text{ kJ/kg})} = 5.6 \text{ kg/min} \quad (\text{"Rule of thumb" answer})$$

Now we return to Step 7 and use more accurate data.

For octane, we'll choose the same reference state. From data in Appendix B:

$$\begin{aligned}\hat{H}_{O,in} &= \int_{373}^{399} C_{p,l} dT + \Delta\hat{H}_{O,v} + \int_{399}^{623} C_{p,v} dT \\ &= (255)(399 - 373) + 34,400 + \int_{399}^{623} (-6.096 + 0.7712T - 4.195 \times 10^{-4} T^2 + 8.855 \times 10^{-8} T^3) dT \\ &= 6630 + 34400 + 64753 = 105783 \text{ J/gmol} = 105.8 \text{ kJ/gmol}\end{aligned}$$

which is equivalent to 928 kJ/kg.

For steam, we'll use the steam tables (note that this a different reference state than what we used for the rough calculations).

$$\hat{H}_{W,in} = 251.7 \text{ kJ/kg (water at } 60^\circ\text{C and 5 bar, by linear interpolation)}$$

$$\hat{H}_{W,out} = 2748.1 \text{ kJ/kg (saturated steam at 5 bar)}$$

Now using these more accurate values in the energy balance equation:

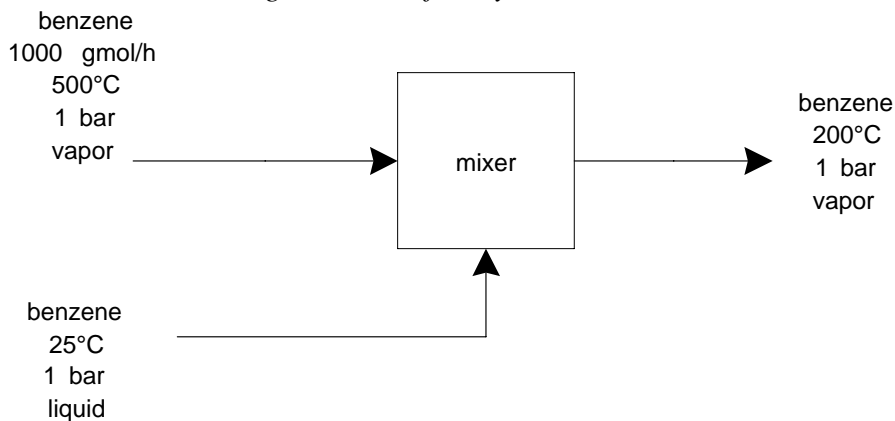
$$\dot{m}_{O,in}(\hat{H}_{O,in} - \hat{H}_{O,out}) = \dot{m}_{W,in}(\hat{H}_{W,out} - \hat{H}_{W,in})$$

$$\dot{m}_{W,in} = 17.1 \text{ kg/min} \frac{(928 \text{ kJ/kg})}{(2748.1 - 251.7 \text{ kJ/kg})} = 6.36 \text{ kg/min ("Accurate" answer)}$$

Given how easy it was to use the rules of thumb (and that we don't need to have access to much data), the answers are surprisingly close. Using the rules of thumb is a good way to check your answers for reasonableness.

P6.46

Steps 1 and 2. Draw a diagram and define system.



The mixer is the system.

Steps 3-5. Choose components, define stream variables, check units, define basis.

Benzene B is the only component. We'll identify the streams as "hot" for the hot inlet, "cold" for the cold inlet, and "out" for the outlet. Units are all consistent. The basis is

$$\dot{n}_{B,hot} = 1000 \text{ gmol/h}$$

Step 6. Set up and solve process flows.

The steady-state material balance equation is:

$$\dot{n}_{B,hot} + \dot{n}_{B,cold} = 1000 + \dot{n}_{B,cold} = \dot{n}_{B,out}$$

Step 7. Define energy of process streams

We'll choose liquid benzene at 1 bar and 25°C as the reference state. From Table B.17 and B.20 we find the data we need to evaluate the enthalpy of the other streams by (a) heating liquid benzene from 25°C to the boiling point temperature of 80.1°C, (b) vaporizing at 80.1°C, and (c) heating vapor from 80.1°C to either 500°C (hot inlet) or 200°C (outlet).

$$\hat{H}_{B,cold} = 0$$

$$\begin{aligned}\hat{H}_{B,hot} &= \int_{298}^{353} (-6.2106 + 0.565T - 3.141 \times 10^{-4} T^2) dT + 30700 \\ &\quad + \int_{353}^{773} (-33.92 + 0.4739T - 3.017 \times 10^{-4} T^2 + 7.13 \times 10^{-8} T^3) dT \\ &= 7939 + 30700 + 61872 = 100,511 \text{ J/gmol} = 100.5 \text{ kJ/gmol} \\ \hat{H}_{B,out} &= \int_{298}^{353} (-6.2106 + 0.565T - 3.141 \times 10^{-4} T^2) dT + 30700 \\ &\quad + \int_{353}^{573} (-33.92 + 0.4739T - 3.017 \times 10^{-4} T^2 + 7.13 \times 10^{-8} T^3) dT \\ &= 7939 + 30700 + 27958 = 66,597 \text{ J/gmol} = 66.6 \text{ kJ/gmol}\end{aligned}$$

Step 8. Identify heat and work.

None.

Step 9. Define changes in system energy

None – system is at steady state.

Steps 10-12: Write energy balance, solve, check.

The steady-state differential energy balance, with no heat or work terms, is simply:

$$\sum_{in} \dot{n}_j \hat{H}_j - \sum_{out} \dot{n}_j \hat{H}_j = 0$$

$$\dot{n}_{B,hot} \hat{H}_{B,hot} + \dot{n}_{B,cold} \hat{H}_{B,cold} = \dot{n}_{B,out} \hat{H}_{B,out}$$

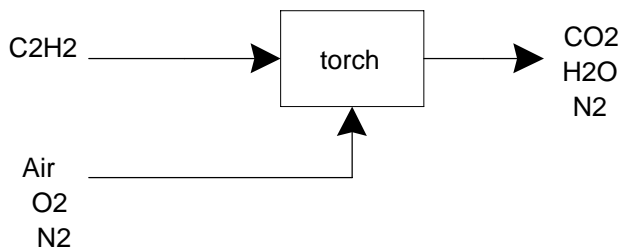
Substituting in the known values:

$$(1000 \text{ gmol/h})(100.5 \text{ kJ/gmol}) + \dot{n}_{B,cold}(0) = (1000 + \dot{n}_{B,cold})(66.6 \text{ kJ/gmol})$$

$$\dot{n}_{B,cold} = 509 \text{ gmol/h}$$

P6.47

Steps 1 and 2. Draw a diagram and define system.



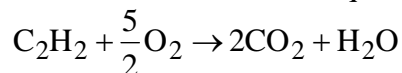
Combustion of acetylene produces CO_2 and H_2O . Since oxygen is fed in stoichiometric quantity, and acetylene is completely combusted, no oxygen leaves the torch. The system is the torch and its contents.

Steps 3-5. Choose components, define stream variables, check units, define basis.

Components are acetylene (A), oxygen (O), nitrogen (N), carbon dioxide (C) and water (W). Stream variables will be defined as “in” or “out”. We are not given a basis, so we’ll choose one: $\dot{n}_{A,in} = 100 \text{ gmol/h}$. We’ll work in kJ and in gmol.

Step 6. Set up and solve process flows.

The balanced chemical reaction equation is



From the specification of stoichiometric feed ratio:

$$\dot{n}_{O,in} = 250 \text{ gmol/h}$$

Since air is 21 mol% O_2 and 79 mol% N_2 :

$$\dot{n}_{N,in} = \left(\frac{79}{21}\right)250 = 940.5 \text{ gmol/h} = \dot{n}_{N,out}$$

From a steady-state balance on the torch, given the stoichiometry and 100% conversion,

$$\dot{m}_{C,out} = 200 \text{ gmol/h}$$

$$\dot{m}_{W,out} = 100 \text{ gmol/h}$$

Step 7. Define energy of process streams.

Only enthalpy changes are of interest. One choice for a reference state is the elements in their normal state of aggregation and at 298 K and 1 atm. This is convenient when we have a chemical reaction because we can then use enthalpy of formation data. Another convenient choice is the combustion products: $\text{CO}_2(\text{g})$, $\text{H}_2\text{O}(\text{g})$, and $\text{N}_2(\text{g})$ at 298 K and 1 atm. By choosing this reference state, we can use the enthalpy of combustion data. Let's work with the latter.

We'll assume the acetylene and air in the inlet stream are at 298 K (close to room temperature). From the data in Table B.3:

$$\hat{H}_{A,in} = -\Delta\hat{H}_{c,A}^\circ = 1257 \text{ kJ/gmol}$$

$$\hat{H}_{O,in} = 0 \text{ kJ/gmol}$$

$$\hat{H}_{N,in} = 0 \text{ kJ/gmol}$$

The outlet stream is at the adiabatic flame temperature T_f . The compounds in the stream are all in the gas phase, so they differ from the reference state only in temperature and we calculate the enthalpy at T_f by using C_p . We should really use the polynomial expressions but since this is just a relative calculation anyway (we are comparing acetylene relative to methane), we'll be very lazy and use approximate C_p 's. We also neglect any enthalpy of mixing.

$$\hat{H}_{C,out} \approx C_p(T_f - T_{ref}) = \frac{37(T_f - 298)}{1000} = 0.037T_f - 11 \text{ kJ/gmol}$$

$$\hat{H}_{W,out} \approx C_p(T_f - T_{ref}) = \frac{33.6(T_f - 298)}{1000} = 0.0336T_f - 10 \text{ kJ/gmol}$$

$$\hat{H}_{N,out} \approx C_p(T_f - T_{ref}) = \frac{29.1(T_f - 298)}{1000} = 0.029T_f - 8.7 \text{ kJ/gmol}$$

Step 8. Identify heat and work.

This is an adiabatic flame, so there is no heat. Nor is there any work.

Step 9. Define changes in system energy

None - we assume steady state.

Steps 10-12: Write energy balance, solve, check.

$$\sum_{in} \dot{n}_j \hat{H}_j = \sum_{out} \dot{n}_j \hat{H}_j$$

$$(100)(1257) + 250(0) + 940.5(0) = 200(0.037T_f - 11) + 100(0.0336T_f - 10) + 940.5(0.029T_f - 8.7)$$

The solution is

$$T_f \approx 3600 \text{ K for acetylene}$$

If we do the exact same calculation, but for methane (keeping in mind that the stoichiometry is different as well as the enthalpy of combustion, we find

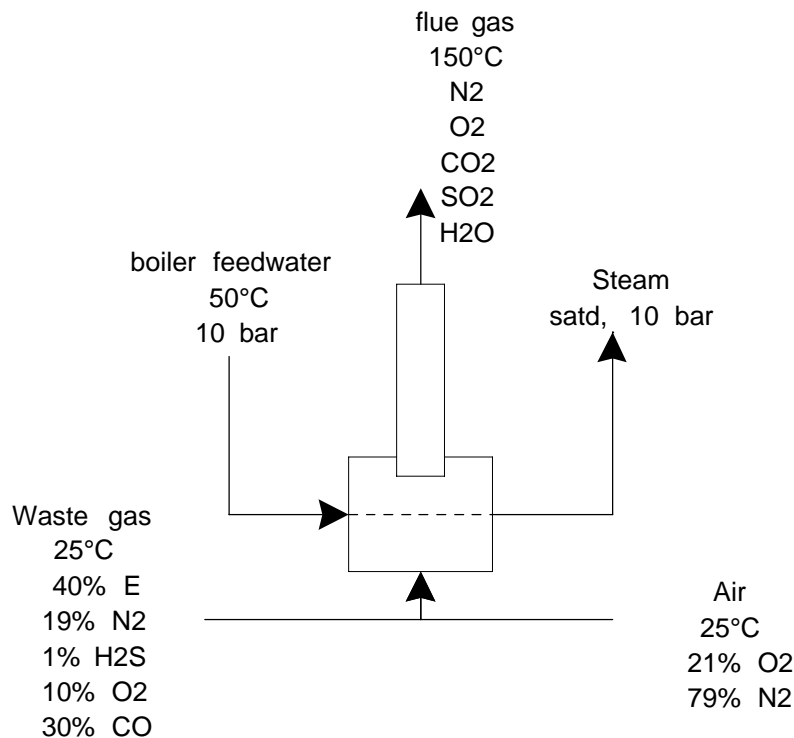
$$T_f \approx 2800 \text{ K for methane}$$

or 800 K cooler.

The approximation of adiabatic operation of the torch is a poor one, as is the neglect of the temperature dependence of the heat capacity. Still, this shows that acetylene torches can reach much higher temperatures than can methane torches. This makes a huge difference, because of the high melting temperatures of many metals.

P6.48

Steps 1 and 2. Draw a diagram and define system.



Air and waste gas mix and are combusted in the firebox of the furnace. Boiler feedwater enters through tubes lining the wall of the furnace, where heat from the fire is transferred to the water, producing steam. We will choose two different systems: first we'll look at the contents of the firebox not including the tubes, and second we'll look at just the

contents of the tubes. (Another appropriate choice is the entire contents of the firebox including the tubes as the system.)

Steps 3-5. Choose components, define stream variables, check units, define basis.

There are many components: oxygen (O), nitrogen (N), hydrogen sulfide (H), sulfur dioxide (S), water (W), carbon monoxide (CM), carbon dioxide (CD) and ethane (E). For units, we'll use gmol for the waste gas, air, and flue gas, and kg for the boiler feedwater and steam. (Mixing the units of mole and mass will not cause us problems, because the streams do NOT mix.) Streams will be defined as "waste", "air", "flue", "bfw" for boiler feedwater, and "steam" for steam. No basis is given, we'll choose 100 gmol/s of waste gas as a convenient basis:

$$\dot{n}_{waste} = 100 \text{ gmol/s}$$

Based on the composition of the waste gas stream, then

$$\dot{n}_{E,waste} = 40 \text{ gmol/s}$$

$$\dot{n}_{N,waste} = 19 \text{ gmol/s}$$

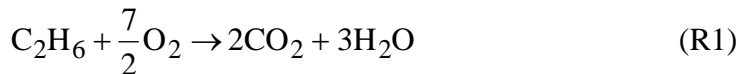
$$\dot{n}_{O,waste} = 10 \text{ gmol/s}$$

$$\dot{n}_{H,waste} = 1 \text{ gmol/s}$$

$$\dot{n}_{CM,waste} = 30 \text{ gmol/s}$$

Step 6. Set up and solve process flows.

Considering only the system of the firebox (excluding the steam/boiler feedwater), we have several reactions to consider:



The stoichiometric flow rate of oxygen required for complete combustion is

$$\left(\frac{7}{2}\right)(40) + \left(\frac{1}{2}\right)(30) + \left(\frac{3}{2}\right)(1) - 10 = 146.5 \text{ gmol/s}$$

Since air is fed at 20% excess,

$$\dot{n}_{O,air} = 1.2 \times 146.5 = 175.8 \text{ gmol/s}$$

$$\dot{n}_{N,air} = \frac{79}{21} 175.8 = 661.3 \text{ gmol/s}$$

From material balance equations on ethane, carbon monoxide, and hydrogen sulfide (assuming complete combustion):

$$\dot{m}_{E,flue} = 0 = 40 - \dot{\xi}_1 \rightarrow \dot{\xi}_1 = 40 \text{ gmol/s}$$

$$\dot{m}_{CM,flue} = 0 = 30 - \dot{\xi}_2 \rightarrow \dot{\xi}_2 = 30 \text{ gmol/s}$$

$$\dot{m}_{H,flue} = 0 = 1 - \dot{\xi}_3 \rightarrow \dot{\xi}_3 = 1 \text{ gmol/s}$$

Finishing the material balance equations:

$$\dot{m}_{CD,flue} = 2\dot{\xi}_1 + \dot{\xi}_2 = 80 + 30 = 110 \text{ gmol/s}$$

$$\dot{m}_{S,flue} = \dot{\xi}_3 = 1 \text{ gmol/s}$$

$$\dot{m}_{W,flue} = 3\dot{\xi}_1 + \dot{\xi}_3 = 120 + 1 = 121 \text{ gmol/s}$$

$$\dot{m}_{N,flue} = \dot{m}_{N,waste} + \dot{m}_{N,air} = 19 + 661.3 = 680.3 \text{ gmol/s}$$

$$\dot{m}_{O,flue} = \dot{m}_{O,waste} + \dot{m}_{O,air} - \frac{7}{2}\dot{\xi}_1 - \frac{1}{2}\dot{\xi}_2 - \frac{3}{2}\dot{\xi}_3 = 10 + 175.8 - 140 - 15 - 1.5 = 29.3 \text{ gmol/s}$$

Step 7. Define energy of process streams

We have some options. Option 1: we start with the waste gas and air at 298 K and 1 atm, calculate the enthalpy change associated with combustion at 298 K, then calculate the enthalpy change associated with increasing the temperature of the flue gases from 298 K to the outlet temperature, 150°C (423 K). Option 2: we start with the elements at 298 K and 1 atm, and calculate enthalpies of compounds at 298 K from enthalpy of formation data, then correct flue gases for the temperature increase. Either option is fine; we'll go with option 1 here.

Here is the useful data (all for water in the vapor phase as the product of combustion)

Ethane: $\Delta H_c^\circ = -1428.6 \text{ kJ/gmol}$

CO: $\Delta H_c^\circ = -283 \text{ kJ/gmol}$

H₂S: $\Delta H_c^\circ = -518.7 \text{ kJ/gmol}$

CO₂: $C_p = 19.80 + 0.07344T - 5.602 \times 10^{-5}T^2 + 1.7115 \times 10^{-8}T^3$

H₂O: $C_p = 32.24 + 0.001924T + 1.055 \times 10^{-5}T^2 - 3.569 \times 10^{-9}T^3$

O₂: $C_p = 29.1 + 0.01158T - 6.076 \times 10^{-6}T^2 + 1.311 \times 10^{-8}T^3$

N₂: $C_p = 31.15 - 0.01357T + 2.680 \times 10^{-5}T^2 - 1.168 \times 10^{-8}T^3$

SO₂: $C_p = 23.85 + 0.06699T - 4.961 \times 10^{-5}T^2 + 1.328 \times 10^{-8}T^3$

$$H_{flue} = \sum_k \dot{\xi}_k \Delta \hat{H}_{c,k} + \sum_i \dot{m}_{i,flue} \int_{T_{in}}^{T_{out}} C_{p,i} dT$$

$$H_{flue} = (40(-1428.6)) + (30(-283)) + (1(-518.7)) \\ + (110(4.97)) + (121(4.72)) + (29.3(3.73)) + (680.3(3.65)) + (1(5.27))$$

$$H_{flue} = -62,400 \text{ kJ/s}$$

Step 8. Identify heat and work.

There is heat that leaves this system (and is transferred to the steam in the tubes), but no work.

Step 9. Define changes in system energy

None – assumed steady state.

Steps 10-12: Write energy balance, solve, check.

$$\dot{H}_{out} - \dot{H}_{in} = \dot{Q} = -62,400 \text{ kJ/s}$$

The heat that leaves this system is transferred to the contents of the tubes. Now we change the system to the tubes and their contents. The energy balance is

$$\dot{H}_{out} - \dot{H}_{in} = \dot{Q} = +62,400 \text{ kJ/s}$$

We can choose a different reference state for the boiler feedwater and steam (because they are in a different system.) Let's use the triple point of water and then get our data from the steam tables.

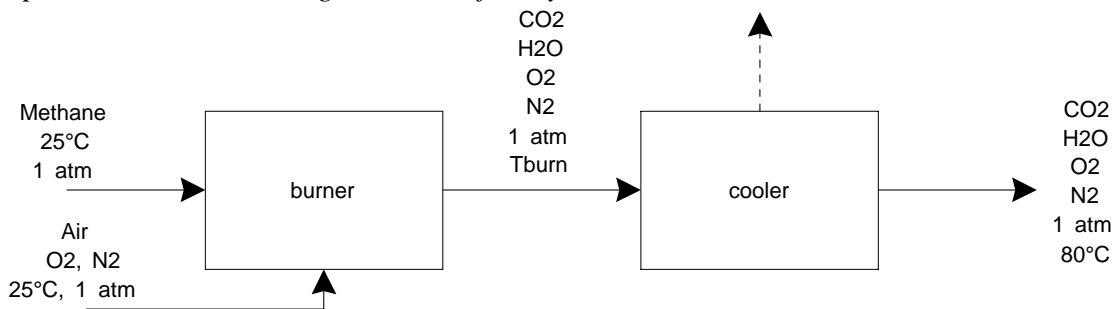
$$\dot{m}_{steam}(\hat{H}_{steam} - \hat{H}_{bfw}) = \dot{m}_{steam}(2777.1 - 210.19) = +62,400 \text{ kJ/s}$$

$$\dot{m}_{steam} = 24.3 \text{ kg/s}$$

Since the basis was 100 gmol/s waste gas, we calculate that we produce 0.243 kg steam per gmol waste gas burned.

P6.49

Steps 1 and 2. Draw a diagram and define system.



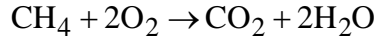
We will use two systems: first the burner, so we can calculate T_{burn} , and next the cooler, so we can determine how much, if any, of the H_2O in the combustion gases is condensed.

Steps 3-5. Choose components, define stream variables, check units, define basis.

Components are methane (M), oxygen (O), nitrogen (N), carbon dioxide (C) and water (W). Streams will be identified as “in”, “out”, or “burn” (for the gases leaving the burner.) No basis is given, we’ll choose $\dot{n}_{M,in} = 100 \text{ gmol/s}$. Units are gmol or J.

Step 6. Set up and solve process flows.

The methane combustion reaction is



From the stoichiometry, the specifications, and the basis we find:

$$\dot{n}_{\text{O},in} = 1.25 \times 2 \times 100 = 250 \text{ gmol/s}$$

$$\dot{n}_{\text{N},in} = \frac{79}{21} \times 250 = 940 \text{ gmol/s}$$

$$\dot{n}_{\text{M},out} = 0 = \dot{n}_{\text{M},in} - \xi = 100 - \xi \rightarrow \xi = 100 \text{ gmol/s}$$

$$\dot{n}_{\text{O},out} = 0 = \dot{n}_{\text{O},in} - 2\xi = 250 - 200 = 50 \text{ gmol/s}$$

$$\dot{n}_{\text{C},out} = \xi = 100 \text{ gmol/s}$$

$$\dot{n}_{\text{W},out} = 2\xi = 200 \text{ gmol/s}$$

$$\dot{n}_{\text{N},out} = \dot{n}_{\text{N},in} = 940 \text{ gmol/s}$$

Step 7. Define energy of process streams

The simplest way to evaluate the enthalpy change is to divide into 2 steps (a) the enthalpy change of combustion of methane at 298 K and (b) the enthalpy change for heating the combustion gases from 298 K to T_{burn} .

Methane: $\Delta H_c^\circ = -802.6 \text{ kJ/gmol}$

CO₂: $C_p = 19.80 + 0.07344T - 5.602 \times 10^{-5}T^2 + 1.7115 \times 10^{-8}T^3$

H₂O: $C_p = 32.24 + 0.001924T + 1.055 \times 10^{-5}T^2 - 3.569 \times 10^{-9}T^3$

O₂: $C_p = 29.1 + 0.01158T - 6.076 \times 10^{-6}T^2 + 1.311 \times 10^{-8}T^3$

N₂: $C_p = 31.15 - 0.01357T + 2.680 \times 10^{-5}T^2 - 1.168 \times 10^{-8}T^3$

$$H_{burn} - H_{in} = \xi \Delta \hat{H}_c + \sum_i \dot{n}_{i,burn} \int_{T_{in}}^{T_{burn}} C_{p,i} dT$$

We do not yet know T_{burn} so cannot evaluate numerically.

Step 8. Identify heat and work.

The burner is adiabatic and there is no mechanical equipment, so $\dot{Q} = \dot{W}_s = 0$

Step 9. Define changes in system energy

Steady-state operation is assumed.

Steps 10-12: Write energy balance, solve, check.

Everything is zero except the enthalpy terms:

$$H_{burn} - H_{in} = 0 = \sum \dot{N}_i \hat{H}_c + \sum_i \dot{N}_{i,burn} \int_{T_{in}}^{T_{burn}} C_{p,i} dT$$

We now solve (using an equation solver) by plugging in the known physical constants and molar flows:

$$T_{burn} = 1970 \text{ K}$$

(This is somewhat cooler than the answer we got for methane in P6.47 – because of the excess air.)

Finally, we are asked to determine whether any of the water condenses in the cooler. This is not an energy balance problem; it is a phase equilibrium problem. At 80°C., from the Antoine equation;

$$\log_{10} P_W^{sat} = 7.96681 - \frac{1668.21}{80 + 228.0} = 2.551$$

$$P_W^{sat} = 355 \text{ mm Hg} = 0.45 \text{ atm}$$

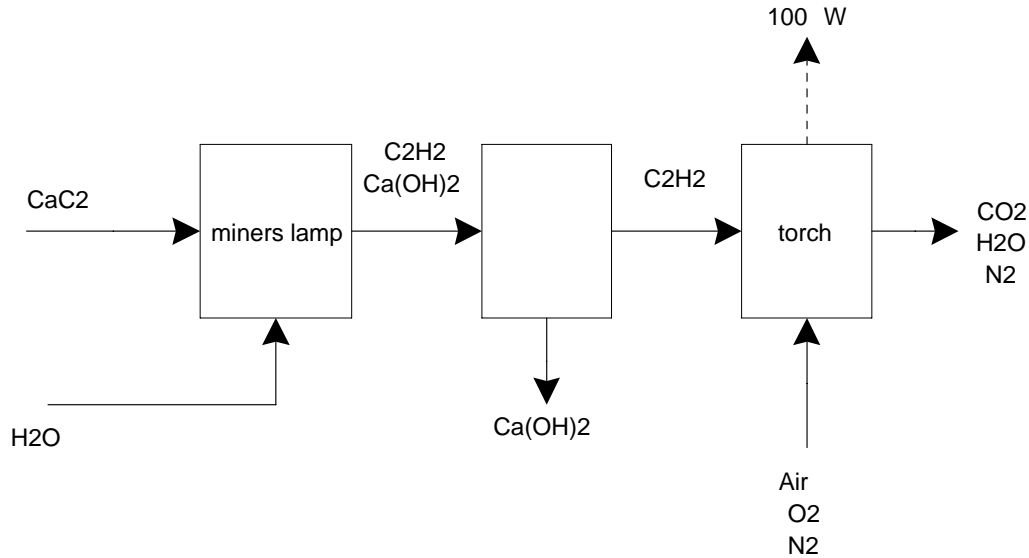
At 100% relative humidity, $y_W P = P_W^{sat} = 0.45 \text{ atm}$, or $y_W = 0.45$. But the water content of the combustion gases is

$$y_W = \frac{\dot{N}_{W,out}}{\dot{N}_{W,out} + \dot{N}_{C,out} + \dot{N}_{O,out} + \dot{N}_{N,out}} = \frac{200}{200 + 100 + 50 + 940} = 0.155$$

In other words, at 80°C the combustion gases are at only 0.155/0.45 or about 34% relative humidity. So none of the water condenses in the cooler. The gases could be cooled even further before the water starts to condense. This would occur when $y_W = 0.155$, $P_W^{sat} = 0.155(1 \text{ atm}) = 0.155 \text{ atm} = 118 \text{ mm Hg}$. From the Antoine equation, we find that this saturation pressure corresponds to 55°C.

P6.50

Steps 1 and 2. Draw a diagram and define system.



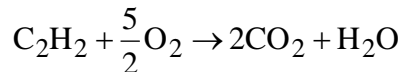
The system is the torch (the last unit of the process). The glow from a torch is due to radiation from the hot combustion gases to the cool air. We need to know how much acetylene must be combusted to produce 100 W. We'll call this "work", even though its not mechanical work. (In a light bulb, electrical work is converted to heat and light.)

Steps 3-5. Choose components, define stream variables, check units, define basis.

Components are acetylene (A), oxygen (O), nitrogen (N), carbon dioxide (C) and water (W). Streams are identified as "in" or "out". We'll work in gmol/s and kJ. The basis is an energy flow: $\dot{W} = 100 \text{ kJ/s}$

Step 6. Set up and solve process flows.

The reaction is



If we assume that air is fed in stoichiometric ratio and that air is 21% oxygen

$$\dot{n}_{\text{O},in} = \frac{5}{2} \dot{n}_{\text{A},in}$$

$$\dot{n}_{\text{N},in} = \frac{79}{21} \dot{n}_{\text{O},in}$$

Assuming complete combustion:

$$\dot{n}_{\text{A},out} = \dot{n}_{\text{A},in} - \xi = 0$$

Step 7. Define energy of process streams

Kinetic and potential energy are neglected. We don't have much information. We'll assume that the reactants leave the torch at 298 K (after giving off light). The change in enthalpy from the inlet to the outlet stream is simply the enthalpy of combustion of acetylene:

$$\dot{H}_{out} - \dot{H}_{in} = \dot{\zeta} \Delta H_c^\circ = -1257 \dot{\zeta} \text{ kJ/s}$$

Step 8. Identify heat and work.

Work is an output, so $\dot{W} = -100 \text{ J/s}$.

Step 9. Define changes in system energy

None – assumed steady state.

Steps 10-12: Write energy balance, solve, check.

$$\dot{H}_{out} - \dot{H}_{in} = -1257 \dot{\zeta} = \dot{W} = -0.1 \text{ kJ/s}$$

$$\dot{\zeta} \cong 8 \times 10^{-5} \text{ gmol/s}$$

Since the rate of reaction equals the flow rate of acetylene to the torch, and one gmole of acetylene is generated per gmol calcium carbide consumed, then the reaction rate of the miner's lamp is also $8 \times 10^{-5} \text{ gmol/s}$. About 150 g of CaC_2 would be sufficient to supply light for an 8-hour work day.

P6.51

Use $C_p = 124.4 \text{ J/mol } ^\circ\text{C}$ for liquid acetic acid from App. B. To heat acetic acid from 50°C to 170°C requires

$$\dot{Q} = 1000 \text{ kmol/h} (124.4 \text{ kJ/kmol } ^\circ\text{C}) (170^\circ\text{C} - 50^\circ\text{C}) = 14,928,000 \text{ kJ/h}$$

The heat is supplied by condensing saturated steam at 10 bar. From steam tables,

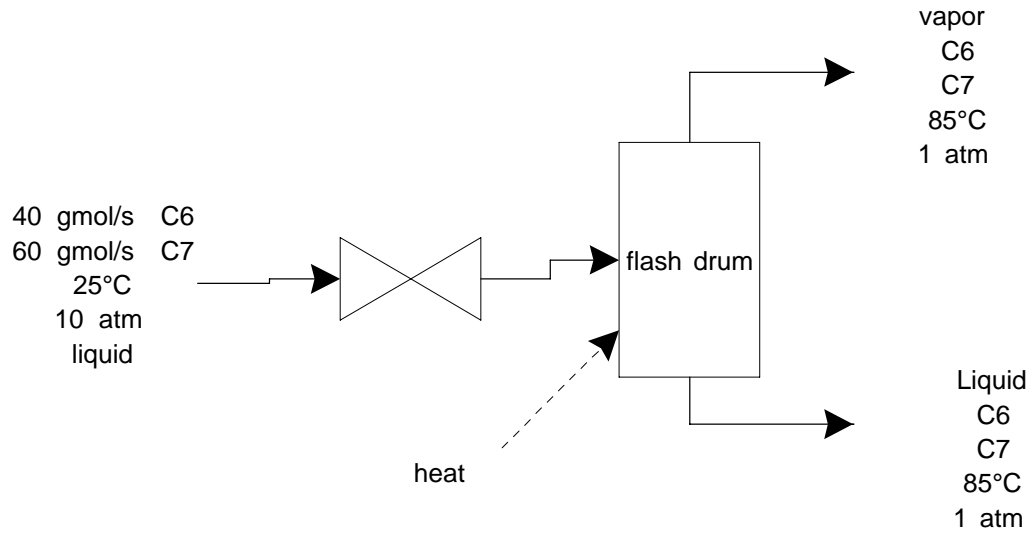
$$\dot{Q} = -14,928,000 = m_{steam} (762.52 - 2777.1) = 2014.48 m_{steam}$$

$$m_{steam} = 7410 \text{ kg/h}$$

At 5 bar, saturated steam is only 151°C , not warm enough to heat the acetic acid to the target temperature.

P6.53

This problem reviews phase equilibrium material from Chapter 5 in addition to covering material from Chapter 6.



Components are hexane (C6) and heptane (C7). System will be the expansion valve plus flash drum. There are 3 streams: feed (f), vapor (v) and liquid (l).

The compositions of the vapor and liquid streams are related by phase equilibrium. From Antoine equation, at 85°C,

$$P_{C6}^{sat} = 1232 \text{ mm Hg}$$

$$P_{C7}^{sat} = 503.5 \text{ mm Hg}$$

Raoult's law is an acceptable model equation.

$$y_{C6}P = x_{C6}P_{C6}^{sat} \rightarrow y_{C6} = x_{C6}\left(\frac{1232}{760}\right) = 1.621x_{C6}$$

$$y_{C7}P = x_{C7}P_{C7}^{sat} \rightarrow y_{C7} = x_{C7}\left(\frac{503.5}{760}\right) = 0.6625x_{C7}$$

Combining these equations with

$$y_{C6} + y_{C7} = 1$$

$$x_{C6} + x_{C7} = 1$$

We solve to find

$$y_{C6} = 0.571, y_{C7} = 0.429$$

$$x_{C6} = 0.353, x_{C7} = 0.647$$

The steady-state differential material balance equations are:

$$40 = 0.571\dot{N}_v + 0.353\dot{N}_l$$

$$60 = 0.429\dot{N}_v + 0.647\dot{N}_l$$

which we solve simultaneously to find:

$$\dot{N}_v = 21.7 \text{ gmol/s}$$

$$\dot{N}_l = 78.3 \text{ gmol/s}$$

The steady-state differential energy balance equation is:

$$\dot{Q} = \dot{H}_v + \dot{H}_l - \dot{H}_f$$

We set the pure components at the feed condition (liquid, 25°C, 10 atm) as the reference state.

To calculate the enthalpy of the liquid stream we

- (i) decrease pressure of liquid from 10 to 1 atm ($\Delta H \sim 0$)
- (ii) increase temperature of 27.64 gmol/s liquid hexane from 25°C to 85°C
- (iii) increase temperature of 50.66 gmol/s liquid heptane from 25°C to 85°C
- (iv) mix hexane and heptane ($\Delta H \sim 0$)

$$\dot{H}_l = 27.64(189.1)(85 - 25) + 50.66(212)(85 - 25) = 958,000 \text{ J/s} = 958 \text{ kJ/s}$$

To calculate the enthalpy of the vapor stream we

- (i) decrease pressure of liquid from 10 to 1 atm ($\Delta H \sim 0$)
- (ii) increase temperature of 12.36 gmol/s liquid hexane from 25°C to 68.74°C, vaporize at 68.74°C, and increase temperature of vapor from 68.74°C to 85°C.
- (iii) increase temperature of 9.34 gmol/s liquid heptane from 25°C to 98.4°C, vaporize at 98.4°C, and decrease temperature of vapor from 98.4°C to 85°C.
- (iv) mix hexane and heptane ($\Delta H \sim 0$)

$$\begin{aligned} \dot{H}_v &= 12.36((189.1)(68.74 - 25) + 28,900 + 143.1(85 - 68.74)) \\ &\quad + 9.34[(212)(98.4 - 25) + 31,800 + 165.9(85 - 98.4)] \\ &= 910,000 \text{ J/s} = 910 \text{ kJ/s} \end{aligned}$$

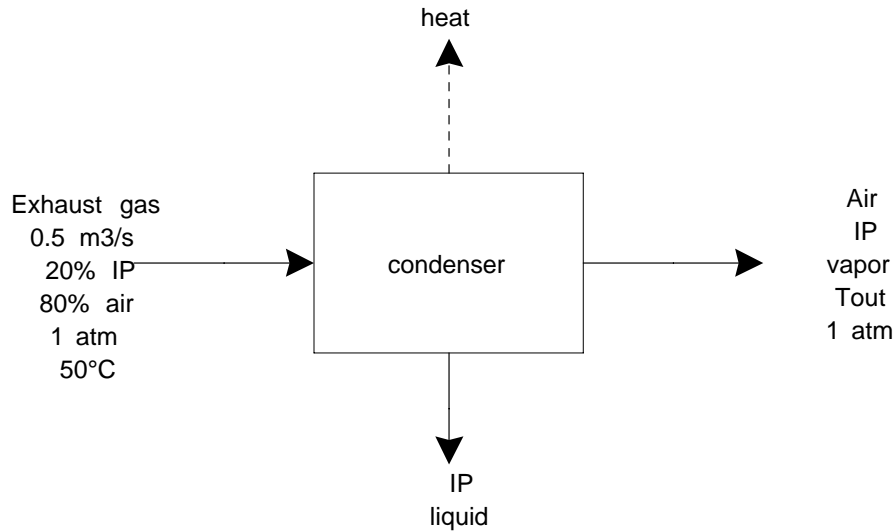
(Even though the molar flow rate of the vapor stream is much smaller than that of the liquid stream, the enthalpy flow of vapor and liquid streams are similar.)

Now we find

$$\dot{Q} = 910 + 958 - 0 = 1868 \text{ kJ/s}$$

P6.54

(a)



We use the ideal gas law to convert the volumetric flow to a molar flow

$$\dot{n}_{in} = \frac{PV}{RT} = \frac{(1 \text{ atm})(500,000 \text{ cm}^3/\text{s})}{(82.057)(50 + 273)} = 18.9 \text{ gmol/s}$$

Therefore

$$\dot{n}_{IP,in} = 0.2 \times 18.9 = 3.77 \text{ gmol/s}$$

$$\dot{n}_{air,in} = 0.8 \times 18.9 = 15.1 \text{ gmol/s}$$

99% of the isopropanol is to be recovered in the liquid.

$$\dot{n}_{IP,liq} = 0.99 \times 3.77 = 3.73 \text{ gmol/s}$$

$$\dot{n}_{IP,vapor} = 0.01 \times 3.77 = 0.0377 \text{ gmol/s}$$

All the air exits in the vapor stream

$$\dot{n}_{air,vapor} = 15.1 \text{ gmol/s}$$

The mole fraction isopropanol in the vapor stream is

$$y_{IP} = \frac{\dot{n}_{IP,vapor}}{\dot{n}_{IP,vapor} + \dot{n}_{air,vapor}} = \frac{0.0377}{0.0377 + 15.1} = 0.0025$$

The liquid and vapor streams are at the same temperature. Raoult's law and the Antoine equation are used to determine the temperature at which the mole fraction in the vapor phase is 0.0025.

$$y_{IP}P = P_{IP}^{sat} = 0.0025(760 \text{ mm Hg}) = 10^{(8.11778 - 1580.92/(T + 219.61))}$$

$$T = -17^\circ\text{C}$$

Very cold!

The energy balance equation is

$$\dot{n}_{liq}\hat{H}_{liq} + \dot{n}_{vap}\hat{H}_{vap} - \dot{n}_{exhaust}\hat{H}_{exhaust} = \dot{Q}$$

We have the temperature, pressure, phase, and flows of all streams, so we just need to calculate enthalpies. Choosing the inlet conditions (50°C, 1 atm, vapor phase) as the reference state and neglecting any enthalpy of mixing:

To find the enthalpy of the condensate we

- (a) heat isopropanol vapor from 50°C to 82.3°C (its normal boiling point)
- (b) condense isopropanol at 82.3°C and 1 atm
- (c) cool isopropanol liquid from 82.3°C to -17°C.

To find the enthalpy of the vapor we

- (a) cool isopropanol vapor from 50°C to -17°C
- (b) cool air from 50°C to -17°C.

Because the temperature changes are moderate, approximate heat capacities are okay.

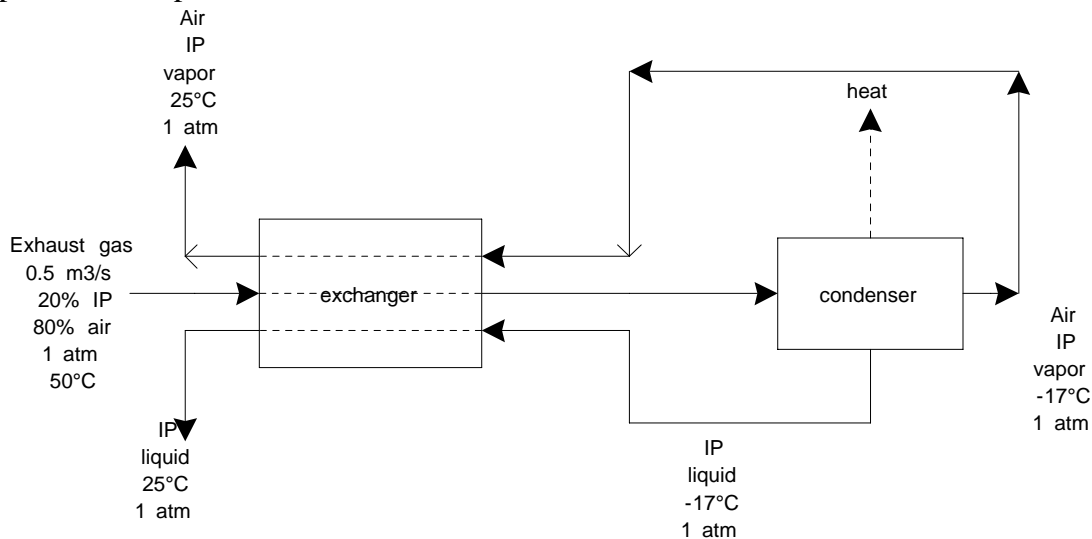
$$\hat{H}_{liq} = 80(82.3 - 50) + (-39,900) + 155((-17) - 50) = -47,700 \text{ J/gmol}$$

$$\hat{H}_{IP,vap} = 80((-17) - 50) = -5360 \text{ J/gmol}$$

$$\hat{H}_{air,vap} = 29((-17) - 50) = -1940 \text{ J/gmol}$$

$$3.73(-47,700) + 0.04(-5360) + 15.1(-1940) = \dot{Q} = -207,400 \text{ J/s} = -207.4 \text{ kJ/s}$$

(b) The very cold isopropanol and air could be used to provide some of the cooling. One possible set-up is:



The dashed lines through the exchanger indicate flow of material, but the material does not mix. Although a very low temperature is required to condense the isopropanol vapor out of the exhaust gases, the pure isopropanol is liquid to much higher temperatures, so it can be warmed to 25°C and still remain liquid. (The heat exchange between the exhaust gas, the liquid, and the cleaned air could also be carried out in two separate exchangers.)

If the entire process is now considered the system:

$$\hat{H}_{liq} = 80(82.3 - 50) + (-39,900) + 155((25) - 50) = -41,200 \text{ J/gmol}$$

$$\hat{H}_{IP,vap} = 80(25 - 50) = -2000 \text{ J/gmol}$$

$$\hat{H}_{air,vap} = 29(25 - 50) = -725 \text{ J/gmol}$$

$$3.73(-41,200) + 0.0377(-2000) + 15.1(-725) = \dot{Q} = -164,700 \text{ J/s} = -164.7 \text{ kJ/s}$$

Cooling duty has dropped by about 20%.

P6.55

With the hydrogen, we are sure that there is at least some vapor. To determine the phase of the material at 200°C and 1 atm, we will have to model the vapor-liquid equilibrium. We'll assume Raoult's law applies to lactic acid and water (although this is questionable given interactions between lactic acid and water). We calculate saturation pressures at 200°C from Antoine's equation.

$$\log_{10} P_{LA}^{sat} = 8.06 - \frac{1823.7}{200 + 134} = 2.60, \quad P_{LA}^{sat} = 398 \text{ mm Hg}$$

$$\log_{10} P_W^{sat} = 7.96681 - \frac{1668.21}{200 + 228} = 4.07, \quad P_W^{sat} = 11,725 \text{ mm Hg}$$

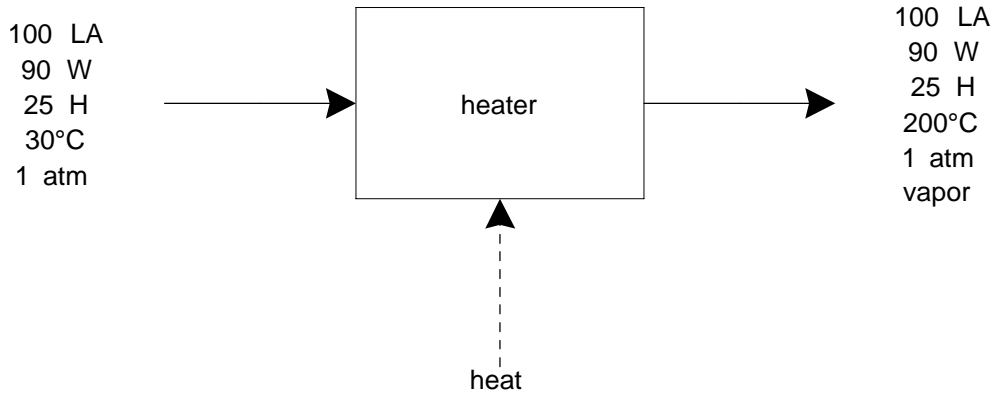
$$x_{LA} = \frac{y_{LA}P}{P_{LA}^{sat}} = \frac{0.4651(760)}{398} = 0.888$$

Assuming we are at the dewpoint:

$$x_W = \frac{y_W P}{P_W^{sat}} = \frac{0.4186(760)}{11725} = 0.027$$

$x_{LA} + x_W = 0.888 + 0.027 = 0.915 < 1$. This result indicates that the pressure would need to be higher for there to be a liquid phase present – so therefore the stream is superheated vapor.

We now sketch the flow diagram and complete energy calculations. Flow rates are shown in gmol/min.



The input stream is a mix of liquid (LA + W) and vapor (H). The steady-state differential energy balance equation

$$\dot{Q} = \dot{n}_{out} \hat{H}_{out} - \dot{n}_{in} \hat{H}_{in}$$

We neglect any enthalpy of mixing and postulate a pathway from “in” to “out”:

- (a) increase temperature of hydrogen from 30°C to 200°C
- (b) increase temperature of liquid water from 30°C to 100°C, vaporize water at 100°C, then increase temperature of water vapor from 100°C to 200°C
- (c) increase temperature of liquid lactic acid from 30°C to 217°C, vaporize lactic acid at 217°C, then decrease temperature of lactic acid vapor from 217°C to 200°C.

Data:

Water: $\Delta \hat{H}_v = 40,650 \text{ J/gmol}$

$C_{p,liq} = 75.4 \text{ J/gmol } ^\circ\text{C}$, $C_{p,vap} = 33.6 \text{ J/gmol } ^\circ\text{C}$,

Lactic acid: $\Delta \hat{H}_v = 63,400 \text{ J/gmol}$

$C_{p,liq} = 262 \text{ J/gmol } ^\circ\text{C}$, $C_{p,vap} = 145 \text{ J/gmol } ^\circ\text{C}$,

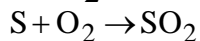
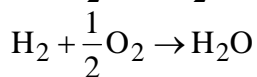
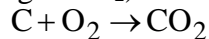
Hydrogen: $C_{p,vap} = 29.1 \text{ J/gmol } ^\circ\text{C}$

$$\begin{aligned} \dot{Q} = & 25(29.1)(200 - 30) + 90((75.4)(100 - 30) + 40650 + (33.6)(200 - 100)) \\ & + 100((262)(217 - 30) + 63400 + (145)(200 - 217)) \end{aligned}$$

$$\dot{Q} = 123,675 + 4,435,920 + 10,992,900 = 15,552,500 \text{ J/min} = 259 \text{ kW}$$

P6.56

1 kg (1000 g) of grains contains: 144 g C (12 gmol C), 62 g H (31 gmol H₂), 788 g O (24.625 gmol O₂) and 6 g S (0.1875 gmol S). Combustion reactions are:



Complete combustion would require $(12 + 1/2(31) + 0.1875 = 27.69 \text{ gmol O}_2$, almost all of which can be supplied by the grains. The enthalpy of each reaction equals the enthalpy of formation of CO_2 , H_2O and SO_2 , respectively (from Table B.3). For 1000 g of grain (assumes water product is vapor), we have

$$\Delta H_c^\circ = 12(-393.5) + 31(-241.83) + 0.1875(-296.81) = -12,300 \text{ kJ}$$

Compare to 1000 g (62.5 gmol) of methane (CH_4):

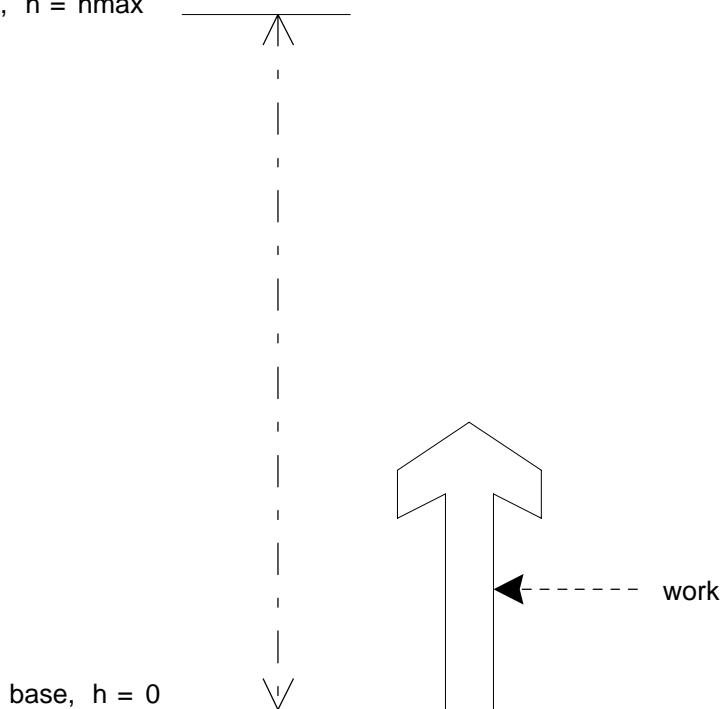
$$\Delta H_c^\circ = 62.5(-802.6) = -50,160 \text{ kJ}$$

The heating value of the grains is only about 25% that of methane, because the grain contains so much oxygen. However, the grains are free whereas the methane must be paid for, and the heating value is high enough to be of interest.

This estimate is an upper limit on the heating value of these grains. The grains are not C, H_2 , etc but complex carbohydrates and alcohols. Most of these compounds (e.g., ethanol, lactic acid, glucose) have large negative enthalpies of formation, whereas the pure elements have enthalpies of formation of zero. The negative enthalpy of formation is multiplied by a negative stoichiometric coefficient to give a positive contribution to the enthalpy of combustion – thus making its absolute value smaller.

P6.57

max, $h = h_{\text{max}}$



Consider the rocket (without the engine) as the system. Initially the velocity is zero and the height $h = 0$. Then imagine that work is done on the system by the gasoline engine, equivalent to the energy released by combustion of the gasoline. (This is overly optimistic – energy released from chemical reactions are not converted to work with

100% efficiency because some heat is generated as well.) Finally, the rocket reaches the apex of its flight, at $h = h_{\max}$, where again its velocity is zero. The rocket itself does not change (much) in temperature, pressure, or phase, so the integral energy balance equation is

$$W = E_{p,sys,f} - E_{p,sys,0} = mg(h_{\max} - 0)$$

The work supplied by combustion is

$$W = 0.005 \text{ gal} \times 125,000 \text{ kJ/gal} = 625 \text{ kJ}$$

Therefore, given a 20 lb rocket:

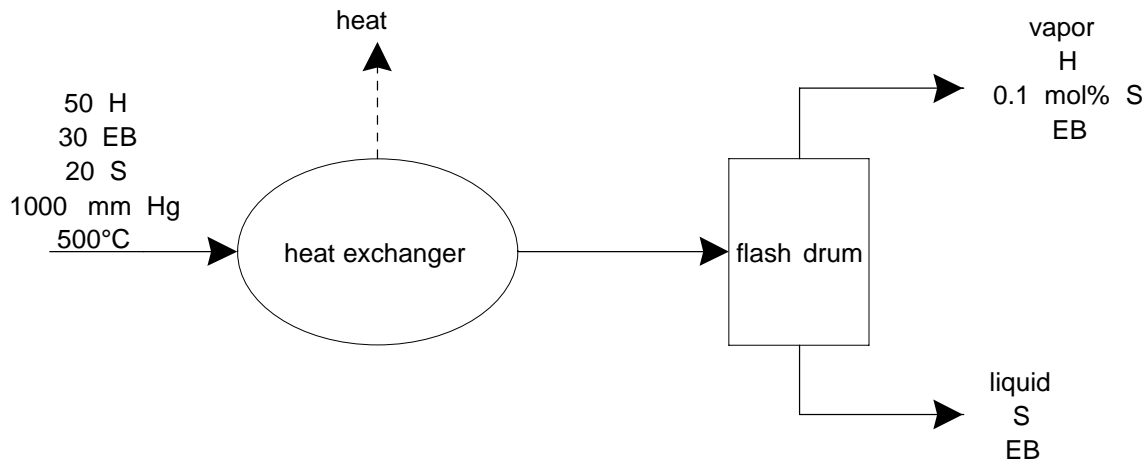
$$625 \text{ kJ} = 625,000 \text{ J} = 625,000 \text{ kg m}^2/\text{s}^2 = \left(\frac{20 \text{ lb}}{2.2 \text{ lb/kg}} \right) \times 9.80 \text{ m/s}^2 \times h_{\max}$$

$$h_{\max} \approx 7000 \text{ m} \approx 23,000 \text{ ft}$$

(Commercial jetliners cruise at around 30,000 to 35,000 ft.)

P6.58

This problem reviews material on phase equilibrium from Chapter 5.



The system will be the combined contents of the heat exchanger plus flash drum. There is one “in” stream and two out streams, which will be designated as “v” for vapor and “l” for liquid. Components are H for hydrogen, EB for ethylbenzene, and S for styrene. Hydrogen can be considered a noncondensable gas, so all of it ends up in the vapor stream:

$$\dot{n}_{H,in} = 50 \text{ gmol/s} = \dot{n}_{H,v} \text{ (at steady state)}$$

Ethylbenzene and styrene are present in both vapor and liquid, and their compositions are related by Raoult’s law.

$$y_S P = x_S P_S^{sat}$$

$$y_{EB} P = x_{EB} P_S^{sat}$$

with

$$\log_{10} P_S^{sat} = 7.14016 - \frac{1574.51}{T + 224.09}$$
$$\log_{10} P_{EB}^{sat} = 6.95719 - \frac{1424.255}{T + 213.21}$$

We also know from the stream composition specification that

$$y_S = 0.001$$

and also that

$$P = 1000 \text{ mm Hg}$$
$$x_S + x_{EB} = 1$$
$$y_S + y_{EB} + y_H = 1$$

From material balance equations:

$$y_S \dot{N}_v + x_S \dot{N}_l = 20 \text{ gmol/s}$$
$$y_{EB} \dot{N}_v + x_{EB} \dot{N}_l = 30 \text{ gmol/s}$$
$$y_H \dot{N}_v = 50 \text{ gmol/s}$$

It is possible to solve this system of equations using equation solving software. If we make an astute approximation, though, we can solve it easily “by hand”. The observation is this: there is very little styrene in the vapor phase, and since styrene and ethylbenzene do not differ much in vapor pressure there is not much ethylbenzene in the vapor either. Therefore, virtually all of the styrene and ethylbenzene ends up in the liquid phase, and it is certainly safe to estimate that the styrene:ethylbenzene ratio stays about the same. This allows us to say, with reasonable accuracy,

$$x_S = 0.4, \text{ (and } x_{EB} = 0.6)$$

Now we use this estimate to calculate:

$$P_S^{sat} = \frac{y_S P}{x_S} = \frac{0.001(1000)}{0.4} = 2.5 \text{ mm Hg}$$

From Antoine’s equation, we find that the saturation pressure of styrene is 2.5 mm Hg if the temperature is 9.4°C. This is the required operating temperature of the flash drum.

Now we can estimate the ethylbenzene:

$$P_{EB}^{sat} = 3.6 \text{ mm Hg (from Antoine eqn, given } T = 9.4^\circ\text{C)}$$

$$y_{EB} = \frac{x_{EB} P_{EB}^{sat}}{P} = \frac{0.6(3.6)}{1000} = 0.002$$

Now,

$$y_H = 1 - (y_S + y_{EB}) = 1 - (0.001 + 0.002) = 0.997$$

Therefore:

$$\dot{N}_v = \frac{50}{0.997} = 50.15 \text{ gmol/s}$$

and

$$\dot{N}_l = 100 - \dot{N}_v = 100 - 50.15 = 49.85 \text{ gmol/s}$$

Now we can check our original approximation:

$$y_S \dot{N}_v + x_S \dot{N}_l = 0.001(50.15) + 0.4(49.85) = 19.99 \cong 20 \text{ gmol/s}$$

$$y_{EB} \dot{N}_v + x_{EB} \dot{N}_l = 0.002(50.15) + 0.6(49.85) = 30.01 \cong 30 \text{ gmol/s} \quad \text{looking good!}$$

To calculate the heat removal rate in the heat exchanger, we need the following information:

$$\text{Hydrogen: } C_p = 27.14 + 0.0093T - 1.381 \times 10^{-5} T^2 + 7.645 \times 10^{-9} T^3$$

$$C_{p,v} = -43.10 + 0.7072T - 4.811 \times 10^{-4} T^2 + 1.301 \times 10^{-7} T^3$$

$$\text{Ethylbenzene: } C_{p,l} = 185.6 \text{ J/gmol } ^\circ\text{C}$$

$$\Delta \hat{H}_v = 35,600 \text{ J/gmol at } 136.2^\circ\text{C}$$

$$C_{p,v} = -28.25 + 0.6159T - 4.023 \times 10^{-4} T^2 + 9.935 \times 10^{-8} T^3$$

$$\text{Styrene: } C_{p,l} = 182.6 \text{ J/gmol } ^\circ\text{C}$$

$$\Delta \hat{H}_v = 37,050 \text{ J/gmol at } 145.1^\circ\text{C}$$

The steady-state differential energy balance is

$$\dot{Q} = H_l + H_v - H_{in}$$

To calculate the change in enthalpy between the inlet and outlet streams, we postulate a pathway, assuming no enthalpy of mixing:

(a) Cool 50 gmol/s hydrogen from 500°C (773 K) to 9.4 °C (283 K)

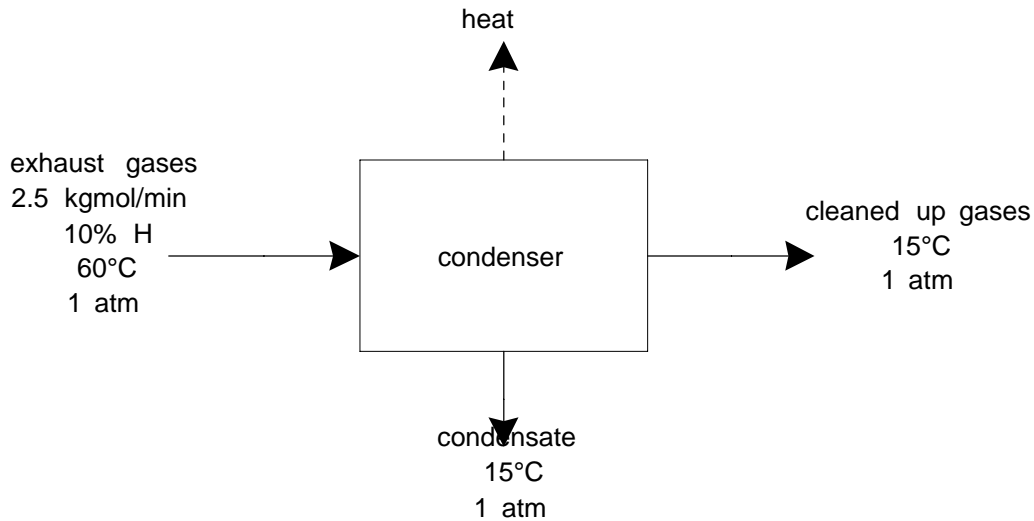
(b) Cool 29.9 gmol/s ethylbenzene vapor from 500°C (773 K) to 136.2°C ((409 K), condense at 409 K, and cool liquid from 409 K to 283 K. Cool remaining 0.1 gmol/s ethylbenzene vapor from 500 K to 283 K.

(c) Cool 19.95 gmol/s styrene vapor from 773 K to 145.1 °C (418 K), condense at 418 K, and cool liquid from 418 K to 283 K. Cool remaining 0.05 gmol/s styrene vapor from 500 K to 283 K.

$$\begin{aligned}\dot{Q} &= 50(-14.35) + 29.9(-84.0 - 35.6 - 23.6) + 0.1(-102.8) + 19.95(-76.1 - 37.05 - 24.8) + 0.05(-95.3) \\ &= -718 + (-4292) + (-2757) = -7767 \text{ kJ/s}\end{aligned}$$

P6.59

At best, the exhaust is cooled to 15°C.



We'll use Raoult's law to calculate the heptane mole fraction in the cleaned up gases, assuming that the condensate is pure heptane.

$$P_H^{sat} = 27 \text{ mm Hg} \text{ from Antoine's equation}$$

$$y_H = \frac{P_H^{sat}}{P} = \frac{27 \text{ mm Hg}}{760 \text{ mm Hg}} = 0.036$$

Since the exhaust gases fed to the condenser are 0.25 kgmol/min heptane and 2.25 kgmol/min air

$$y_H = 0.036 = \frac{\dot{n}_{H,v}}{\dot{n}_{H,v} + \dot{n}_{air,v}} = \frac{\dot{n}_{H,v}}{\dot{n}_{H,v} + 2.25}$$

$$\dot{n}_{H,v} = 0.083 \text{ kgmol/min}$$

The % reduction in heptane in the gases is

$$\frac{0.25 - 0.083}{0.25} \times 100\% = 67\%$$

This decrease is probably not enough to get the heptane concentration below the detection limit or to keep the neighbors from complaining.

The rate of heat removal from the condenser is calculated from the steady-state differential energy balance:

$$\dot{Q} = \dot{H}_l + \dot{H}_v - \dot{H}_f$$

Choosing the feed conditions (vapor, 60°C, 1 atm) as the reference conditions, we calculate the enthalpy of the exiting streams as follows:

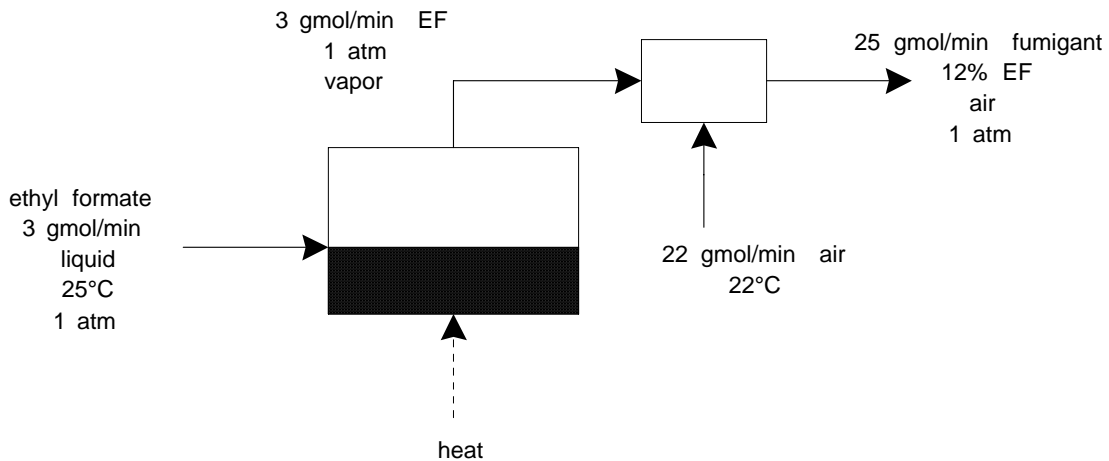
$$\dot{H}_v = 0.083(165.9)(15 - 60) + 2.25(29.1)(15 - 60) = -3570 \text{ kJ/min}$$

$$\begin{aligned}\dot{H}_l &= (0.167)[165.9(98.4 - 60) - 31,800 + (212)(15 - 98.4)] \\ &= -7200 \text{ kJ/min}\end{aligned}$$

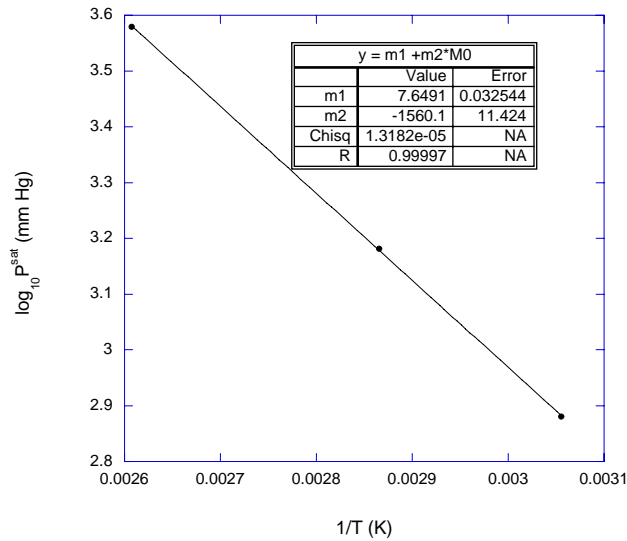
$$\dot{Q} = -7200 - 3570 = -10770 \text{ J/min}$$

P6.60

We imagine a liquid tank into which we pump ethyl formate at room temperature (22°C), which we heat to vaporize. Then the vapors mix with air to make the fumigant.



We don't have constants for the Antoine equation for ethyl formate, but we do have three data points. This isn't enough to reliably fix the 3 constants needed for an Antoine equation (try it using the procedure in Appendix A— you will find you can get multiple values all of which describe the data well.) Instead, we plotted $\log_{10} P^{sat}$ vs $(1/T)$ and fit a straight line.



From this we extrapolate that at room temperature (22°C), the saturation pressure of ethyl formate equals 229 mm Hg or 0.30 atm. Thus, a fumigant containing 12 mol% ethyl formate would be well above the dewpoint and would be all vapor at room temperature. All we need to do is add just enough heat to vaporize the ethyl formate.

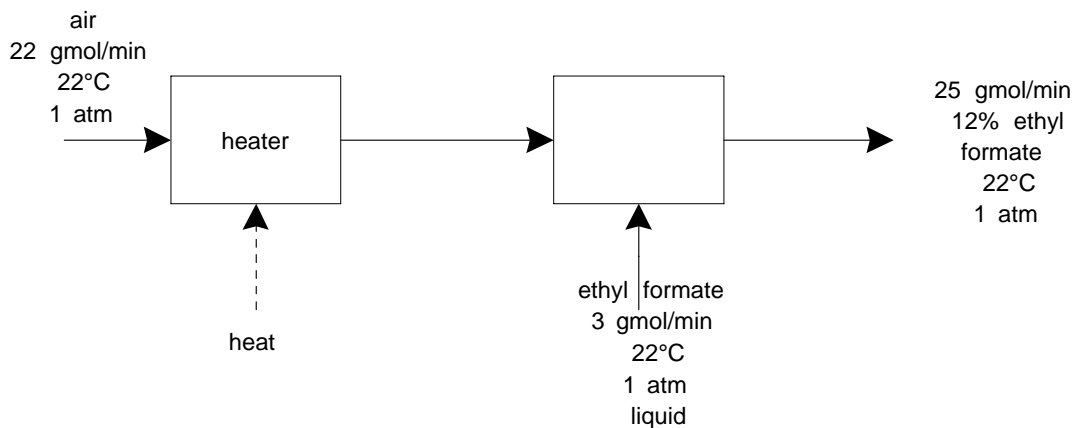
First let's look at the tank heater as the system. The heat required to increase temperature of 3 gmol/min ethyl formate from 22°C to 54.3°C and then to vaporize it is

$$\dot{Q} = \dot{H}_{out} - \dot{H}_{in} = \left(\frac{3 \text{ gmol}}{\text{min}} \times \frac{74 \text{ g}}{\text{gmol}} \right) \left[\frac{0.508 \text{ J}}{\text{g } ^\circ\text{C}} (54.3 - 22) + 97.18 \right] = 25,200 \text{ cal/min}$$

$$\dot{Q} = \frac{25,200 \text{ cal}}{\text{min}} \times \frac{4.184 \text{ J}}{\text{cal}} \times \frac{\text{min}}{60 \text{ s}} \times \frac{\text{W}}{\text{J/s}} = 1760 \text{ W}$$

which is about one moderately powerful hair dryer.

This design will produce a fumigant vapor that is warmer than room temperature. Perhaps a better design would be to heat some of the air, then blow this warm air through the ethyl formate reservoir. The warm air would vaporize some ethyl formate, since ethyl formate has a significant saturation pressure even at room temperature.



Neglecting any dependence on temperature of the enthalpy of vaporization, we quickly calculate from an energy balance on the overall system that 21,600 cal/min, or 1500 W, are required. The air will need to be heated to ~ 165°C; it will then cool as the ethyl formate vaporizes.

P6.61

This problem requires a number of assumptions. Here is one possible answer.

Room volume is $10 \times 12 \times 9 \text{ ft} = 1080 \text{ ft}^3 = 30.6 \text{ m}^3$. Moles of air in room, calculated assuming ideal gas law and 35°C, is

$$n = \frac{PV}{RT} = \frac{1 \text{ atm} \times 30.6 \text{ m}^3 \times (10^6 \text{ cm}^3/\text{m}^3)}{(273 + 35) \times 82.057 \text{ atm cm}^3/\text{gmol K}} = 1210 \text{ gmol}$$

Assume relative humidity is 100%, at 35°C, from Antoine equation

$$\log_{10} P^{sat} = 8.10765 - \frac{1750.286}{235 + 35}$$

or $P^{sat} = 42 \text{ mm Hg}$ and $y_w = P^{sat}/P = 0.0555$. So room air has as much as ~71 gmol water vapor (calculated from $y_w = n_w/(n_w + 1210)$). As room cools, water vapor must be condensed out.

Suppose bucket contains about 1 gal ice, which is about 8 lb or about 4 kg. Melting ice to water is worth 6 kJ/gmol or 333 kJ/kg. C_v of liquid water is 75.4 J/gmol °C or 4.19 kJ/kg.

Assume at end that the room air plus added ice is thermally equilibrated. Room air cools, water vapor condenses, balanced by ice melting and water warming up. The change in internal energy of the ice is:

$$4 \text{ kg} [333 + 4.19(T_f - 0^\circ\text{C})] = 1332 + 16.75T_f$$

The energy change due to condensation of the water vapor is

$\Delta U_v = \Delta H_v - RT_b = 40.7 - 0.008314(373) = 37.6 \text{ kJ/gmol}$. C_v of air = $29.1 + 8.314 = 37.4 \text{ J/gmol } ^\circ\text{C}$ or $0.037 \text{ kJ/gmol } ^\circ\text{C}$. The change in internal energy of the room air is:

$$1210 \text{ gmol} (0.037 \text{ kJ/gmol } ^\circ\text{C}) (T_f - 35^\circ\text{C}) + (-37.6 \text{ kJ/gmol}) \Delta n_w = 44.77T_f - 37.6\Delta n_w - 1567$$

These two expressions must sum to zero to satisfy the energy balance:

$$44.77T_f - 37.6\Delta n_w - 1567 + 1332 + 16.75T_f = 0$$

$$61.5T_f - 235 = 37.6\Delta n_w$$

where Δn_w = the number of moles of water vapor in the air that condenses. This depends on the final temperature, since the equilibrated air will be presumably saturated with water. Procedure: guess T_f , calculate P^{sat} from Antoine equation, then calculate y_w and Δn_w , then see if energy balance is satisfied. Using a spreadsheet, we find

$$T_f = 24.5^\circ\text{C}. \text{ (a comfortable } 76^\circ\text{F)}$$

Perhaps a better way would be to fix the desired temperature (say, 70°F or 21°C) and then find the size of the block of ice that must be melted. About 5.1 kg ice is needed. Not bad! We are neglecting any additional heat input from the outside (due to warm outside walls and poor insulation, air infiltration, or solar radiation) and the thermal mass of the walls and furnishings, but on the other hand we were pessimistic in assuming that the hot air was originally totally saturated with water vapor.

P6.62

The system generates 10 MW electricity. However, due to inefficiencies, there must be a significantly higher input of heat into the system. Given that electricity is 3 to 5 times more expensive than high pressure steam, let's estimate the efficiency of the conversion of steam to electricity at ~ 25%. (Conversion of heat to work is notoriously inefficient.) Thus, roughly 40 MW steam needs to be generated to make 10 MW electricity.

The hot molten salts are used in heat exchangers to heat water to steam. Potassium and sodium nitrates solidify at 333 and 308°C , respectively, so to keep salts molten the temperature must not cool below this. Let's estimate that the salts are cooled from 565 to 350°C in countercurrent exchange with water/steam. The heat capacities of molten potassium and sodium nitrates are 123 and $155.6 \text{ J/gmol } ^\circ\text{C}$, respectively (from Appendix B). We'll use an average of $140 \text{ J/gmol } ^\circ\text{C}$. The flow rate of the molten salts must be

$$\dot{M} \approx \frac{40 \times 10^6 \text{ J/s}}{140 \text{ J/gmol } ^\circ\text{C}(565 - 350^\circ\text{C})} \approx 1300 \text{ gmol/s}$$

The molten salts can be heated to very high temperatures and remain liquid, which has a much greater density (and thus requires much smaller diameter, and hence less expensive, pipes) than would steam.

P6.63

We need to calculate the enthalpy change associated with taking 8500 gmol/h methane and 1500 gmol/h ethane as liquid at 273 K and 260 atm and (1) decreasing P from 260 atm to 1 atm, (2) decreasing T to T_b , (3) vaporizing at T_b , (4) heating vapor to 500 K and (5) increasing P to 50 atm.

Data:

Methane $C_p(\text{gas}) = 19.25 + 0.05213T + 1.197\text{e-}5 T^2 - 1.132\text{e-}8T^3$ (J/mol K)

Ethane $C_p(\text{gas}) = 5.409 + 0.1781T - 6.94\text{e-}5 T^2 + 8.713\text{e-}9T^3$ (J/mol K)

Methane $\Delta\hat{H}_v = 8.535$ kJ/gmol at -161.4°C (112 K)

Ethane $\Delta\hat{H}_v = 14.7$ kJ/gmol at -88.9°C (184 K)

We need heat capacities of liquid. I found for liquid ethane $C_p = 68$ J/gmol K on NIST Chemistry Webbook. This is 2.27 J/g K, and for liquid propane we find $C_p = 2.22$ J/g K, so I assumed C_p for liquid methane is 2.3 J/g K or 37 J/gmol K. The liquid density for methane I found in Lange's Handbook to be 0.42 g/mL at its boiling point. It's larger than that at room temperature, so I just took the density of LNG to be 0.6 g/mL as a rough estimate.

(1) drop liquid from 260 atm to 1 atm at 273 K:

$$\begin{aligned} \Delta H &= mV\Delta P = (8500\text{gmol/h} \times 16\text{g/gmol} + 1500\text{gmol/h} \times 30\text{g/gmol}) \times \frac{1\text{L}}{600\text{g}} \times (1 - 250 \text{ atm}) \\ &\quad \times 1.01325 \times 10^5 \frac{\text{N/m}^2}{\text{atm}} \times \frac{0.001 \text{ m}^3}{\text{L}} \times \frac{\text{kJ}}{1000\text{N/m}^2} \\ &= -7569 \text{ kJ/h} \end{aligned}$$

(2) cool liquid from 273 K to T_b :

$$\Delta H = \sum n C_p \Delta T = 8500 \left(\frac{37}{1000} \right) (112 - 273) + 1500 \left(\frac{68}{1000} \right) (184 - 273) = -59,700 \text{ kJ/h}$$

(3) vaporize at T_b :

$$\Delta H = 8500(8.535) + 1500(14.7) = +94,600 \text{ kJ/h}$$

(4) warm from T_b to 500 K:

$$\Delta H = \sum n \int_{T_b}^{500} C_p dT = 8500(14.33) + 1500(18.34) = +149,300 \text{ kJ/h}$$

(5) increase pressure from 1 atm to 50 atm: $\Delta H = 0$ for ideal gas.

$$\text{Total: } \Delta H = \dot{H}_{out} - \dot{H}_{in} = \dot{Q} = 176,631 \text{ kJ/h}$$

Saturated steam at 30 bars is not on the steam table, but by linear interpolation I find $\Delta \hat{H}_v = 1800 \text{ kJ/kg}$. Therefore total steam required is:

$$\dot{m}_{steam} = \frac{176,600}{1800} = 98 \text{ kg/h}$$

P6.64

In the existing process, condensation of saturated steam at 5 bar is used to evaporate water. Neglecting sensible heat contributions as well as any enthalpy change in the benzoic acid itself (because its mass flow rate is so much less than that of water), to a first approximation, given the enthalpies of vaporization of water at 5 bar and at 1 bar:

$$\dot{m}_{steam} \approx \dot{m}_{evap} \left(\frac{\Delta \hat{H}_{v,1 \text{ bar}}}{\Delta \hat{H}_{v,5 \text{ bar}}} \right) = 3779 \left(\frac{2674.9 - 417.5}{2748.1 - 640.09} \right) = 4050 \text{ kg/h}$$

In the proposed process, benzene rather than water is evaporated. To a first approximation, the steam requirement is calculated from the ratio of the enthalpy of vaporization of benzene/enthalpy of vaporization of steam.

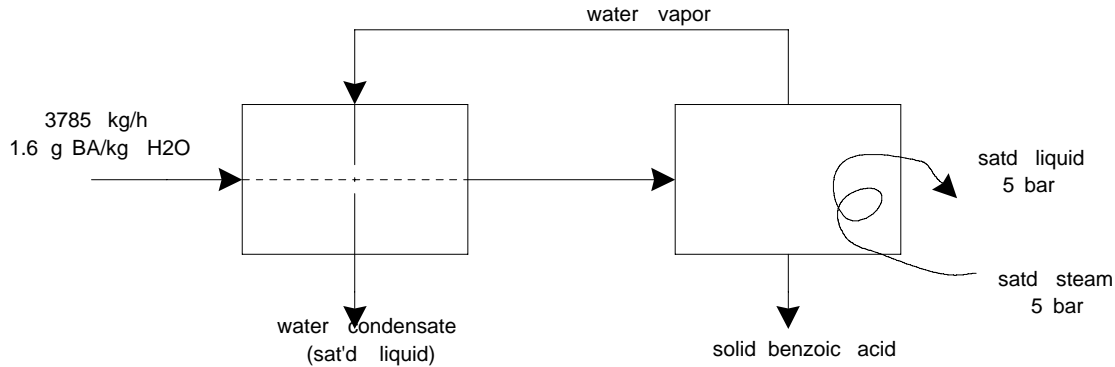
$$\dot{m}_{steam} \approx \dot{m}_{evap} \left(\frac{\Delta \hat{H}_{v,benzene}}{\Delta \hat{H}_{v,5 \text{ bar}}} \right) = 3327 \left(\frac{30.7 \text{ kJ/gmol} \times 1 \text{ gmol/78 g} \times 1000 \text{ g/kg}}{2748.1 - 640.09} \right) = 620 \text{ kg/h}$$

The proposed process requires significantly less energy input, because the enthalpy of vaporization of benzene (kJ/kg) is only about 20% that of water.

The proposed process has some environmental disadvantages as well as some process performance disadvantages. In the existing process, all of the benzoic acid is recovered as a solid. In the proposed process, about 75 g benzoic acid (~1% of total fed) is not recovered. Perhaps of greater concern is the contamination of the water with benzene: per Perry's Handbook the solubility of benzene in water is ~0.7 g benzene/kg water. Thus, in the proposed process, the raffinate stream would contain ~2.6 kg benzene.

The existing process could be improved by energy integration. Rather than injecting cold water to cool and condense the water vapor, a multistage evaporator system should be set up. For example, a two-stage system is diagrammed. The water vapor produced in the second evaporator is sent to the first, which operates at a vacuum. Here, the vapor is

condensed to saturated liquid and the water in the feed stream is partially vaporized. Steam is required in the 2nd unit. Since the waste water stream is presumably at room temperature (roughly 22°C) while the water condensate from the 1st evaporator is saturated and therefore slightly below 100°C, the saturated steam in the second evaporator is required simply to provide the sensible heat for raising the temperature of the liquid water, and not for evaporation. This greatly reduces steam requirements.



P6.65

Complete combustion of 1000 gmol/s C produces 1000 gmol/s CO₂ and uses 1000 gmol/s O₂. The air feed rate is 5952 gmol/s; at 21 mol% O₂ this converts to 1250 gmol/s O₂ (25% excess) plus 470 gmol/s N₂. By material balance the exit gas contains 1000 gmol/s CO₂, 250 gmol/s O₂, and 4702 gmol/s N₂.

With the system chosen as the furnace and heat exchanger excluding the steam tubes, the energy balance is $\dot{H}_{out} - \dot{H}_{in} = \dot{Q}$. To calculate $\dot{H}_{out} - \dot{H}_{in}$, we construct a path of (1) reacting C to CO₂ at 25°C and (2) heating exit gas from 25°C to 100°C.

(1) At 25°C, $\Delta\hat{H}_r = \Delta\hat{H}_{f,CO_2} = -393.5$ kJ/gmol CO₂ (from App. B) or -393,500 kJ/s for 1000 gmol/s basis.

(2) Using approximate values for heat capacities,

$$\left[1000(37) + 250(29.3) + 4700(29.1)\right](100 - 25) \left(\frac{1}{1000}\right) = +13,580 \text{ kJ/s}$$

$$\text{Therefore } \dot{H}_{out} - \dot{H}_{in} = -393500 + 13580 = \dot{Q} = -379,900 \text{ kJ/s}$$

Now changing system to the water/steam in the tubes, the energy balance is still $\dot{H}_{out} - \dot{H}_{in} = \dot{Q}$. Because the heat transferred from the combustion gases is equal to the heat transferred to the steam, we know that $\dot{Q} = +379,900$ kJ/s. From steam tables, at 60 bar the enthalpy change from 50°C to saturated steam is 2570 kJ/kg. Therefore:

$$\begin{aligned} \dot{H}_{out} - \dot{H}_{in} &= \dot{m}_{steam}(2570) = 379,900 \\ \dot{m}_{steam} &= 148 \text{ kg/h} \end{aligned}$$

To calculate the temperature of the combustion gases entering the heat exchanger, we calculate backward, knowing that the water leaving the exchanger is a saturated liquid at 60 bar. From steam tables, the enthalpy change from 50°C to saturated liquid is 999.4 kJ/kg. Therefore, the heat transferred in the exchanger is 148(999.4) or 147,900 kJ/s.

The heat transferred to the water in the exchanger equals the heat transferred from the combustion gases as they cool. Switching to the combustion gases in the exchanger as the system, the energy balance is:

$$\dot{H}_{out} - \dot{H}_{in} = \sum_i \dot{N}_i \int_{100}^{T_{in}} C_{p,i} dT = \dot{Q} = 147,900 \text{ kJ/s}$$

where T_{in} is the temperature of the combustion gases into the exchanger and the summation is evaluated over all the combustion gases. For an approximate answer, we'll use the approximate C_p values:

$$[1000(37) + 250(29.3) + 4700(29.1)](T_{in} - 100) \left(\frac{1}{1000} \right) = +147,900 \text{ kJ/s}$$

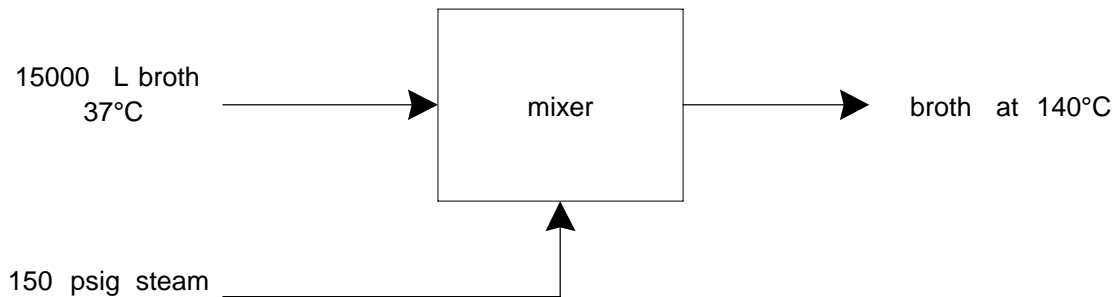
$$T_{in} = 916^\circ\text{C}$$

(With this large temperature change, it would be much better to use the more accurate polynomial expressions for C_p . This gives a polynomial expression in T_{in} ; the root of the equation is found by trial-and-error or by using a spreadsheet solver or other equation solver. Finding the approximate solution first is still a good idea because it is a check of the more accurate solution.)

P6.66

Heat sterilization of broths is carried out under pressure and is sometimes called autoclaving. This way, temperatures that are high enough to kill bacteria and spores are reached without vaporizing the water in the broth. The pressure must be at least 60 psia for the temperature of liquid water to reach 140°C.

In direct injection, steam is injected directly into the broth.



If we assume the broth has physical properties similar to water, then the density is 1 g/mL or 1 kg/L, so

$$m_{broth,in} = 15000 \text{ kg}$$

From a material balance equation

$$m_{broth,out} = 15000 + m_{steam,in}$$

The energy balance equation simplifies to

$$H_{broth,out} - (H_{broth,in} + H_{steam,in}) = 0$$

Let's choose liquid water at 37°C as the reference state (and neglect any pressure effects – the pressure is not stated but must be greater than 60 psia and less than 164.7 psia.

The heat capacity of the broth is taken to be that of water: 4.18 J/g °C. Thus:

$$H_{broth,in} = 0$$

$$\begin{aligned} H_{broth,out} &= m_{broth,out} C_{p,broth} (T_{out} - T_{ref}) \\ &= (15000 + m_{steam,in}) \frac{4.18 \text{ kJ}}{\text{kg } ^\circ\text{C}} (140 - 37^\circ\text{C}) = 430.5(15000 + m_{steam,in}) \end{aligned}$$

For the steam, we imagine a path in which liquid temperature is increased from 37°C to 185°C, then the liquid is vaporized at 185°C (the saturation temperature corresponding to 150 psig). The enthalpy of vaporization at 185°C is 1995 kJ/kg per the NIST Chemistry Webbook.

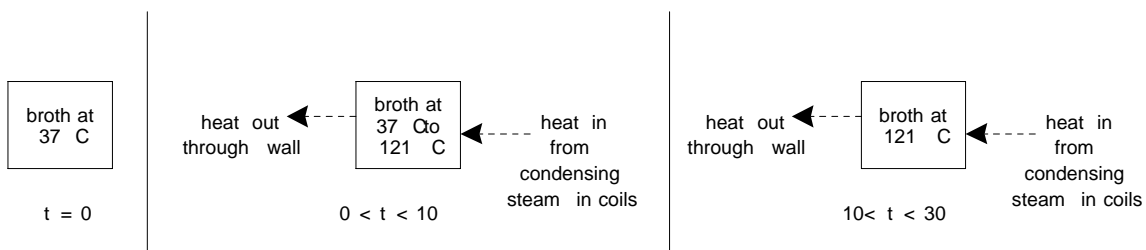
$$H_{steam,in} = m_{steam,in} [(4.18 \text{ kJ/kg}^\circ\text{C})(185 - 37) + 1995] = 2610 m_{steam,in}$$

Inserting into the energy balance:

$$\begin{aligned} 430.5(15000 + m_{steam,in}) &= 2610 m_{steam,in} \\ m_{steam,in} &= 2960 \text{ kg} \end{aligned}$$

Almost 3000 kg steam are condensed in the direct injection method. This dilutes the broth, which may be undesirable.

For the batch sterilization, there are 2 time intervals over which heat is being added and removed:



We consider the contents of the vat as our system (excluding the steam coils). During the second time interval, the temperature is constant at 121°C. There is no change in the system energy, because the temperature is constant. There is no material flowing in or out of the system, and there is no work. Thus the integral energy balance simplifies to:

$$\sum Q = 0$$

In other words, the heat added through the coils is just sufficient to make up for the loss of heat through the uninsulated walls.

$$Q_{in} = - \int_{10}^{30} \dot{Q}_{out} dt = (210 \text{ kJ/min } ^\circ\text{C})(20 \text{ min})(121 - 25^\circ\text{C}) = 403200 \text{ kJ}$$

The heat is supplied by condensing steam, so $m_{steam} = 403200 \text{ kJ}/1995 \text{ kJ/kg} = 202 \text{ kg}$. This is the total steam condensed over 20 minutes, and the rate of heat loss is constant, so the steam flow rate is constant at 10.1 kg/min.

In the first time interval, the broth temperature changes from 37 to 121°C. The unsteady-state differential energy balance is

$$\frac{dU_{sys}}{dt} = \sum \dot{Q}$$

The change in system energy is due to the change in temperature:

$$\frac{dU_{sys}}{dt} = \frac{d[m_{sys}C_v(T_{sys} - T_{ref})]}{dt} = m_{sys}C_v \frac{dT_{sys}}{dt} = 15000(4.18) \frac{dT_{sys}}{dt} = 62700 \frac{dT_{sys}}{dt}$$

There is heat input from the steam condensing in the coils, and heat output through the wall

$$\sum \dot{Q} = \dot{m}_{steam} \Delta \hat{H}_v - (210)(T_{sys} - 25) = 1995 \dot{m}_{steam} - 210 T_{sys} + 5250$$

$$31.43 \frac{dT_{sys}}{dt} + 0.105 T_{sys} - 2.63 = \dot{m}_{steam}$$

To proceed, we need to consider how the vat is operated and controlled during the unsteady-state interval. Two possibilities are: (1) the temperature profile is linear or (2) the steam flow rate is constant. (There are other possible control configurations as well. These two are the simplest.) Let's consider each in turn.

(1) *If the temperature profile is linear.*

$$\frac{dT_{sys}}{dt} = \frac{121 - 37^\circ\text{C}}{10 \text{ min}} = 8.4 \text{ } ^\circ\text{C/min}$$

$$T_{sys} = 37 + 8.4t$$

We insert these expressions into our energy balance equation:

$$31.43(8.4) + 0.105(37 + 8.4t) - 2.63 = \dot{m}_{steam}$$

$$\dot{m}_{steam} = 265.3 + 0.88t$$

The total steam consumed over this 10 minute time interval is

$$m_{steam} = \int_0^{10} \dot{m}_{steam} dt = \int_0^{10} (265.3 + 0.88t) dt = 2700 \text{ kg}$$

The total steam required for the warmup plus sterilization period is 2900 kg.

(2) *If the steam condensation rate is constant.*

In this case we have a linear first-order differential equation with constant coefficients

$$31.43 \frac{dT_{sys}}{dt} + 0.105T_{sys} = 2.63 + \dot{m}_{steam}$$

The general solution to this equation is

$$T_{sys} = \frac{9.464(2.63 + \dot{m}_{steam})e^{0.00334t} + C}{e^{0.00334t}}$$

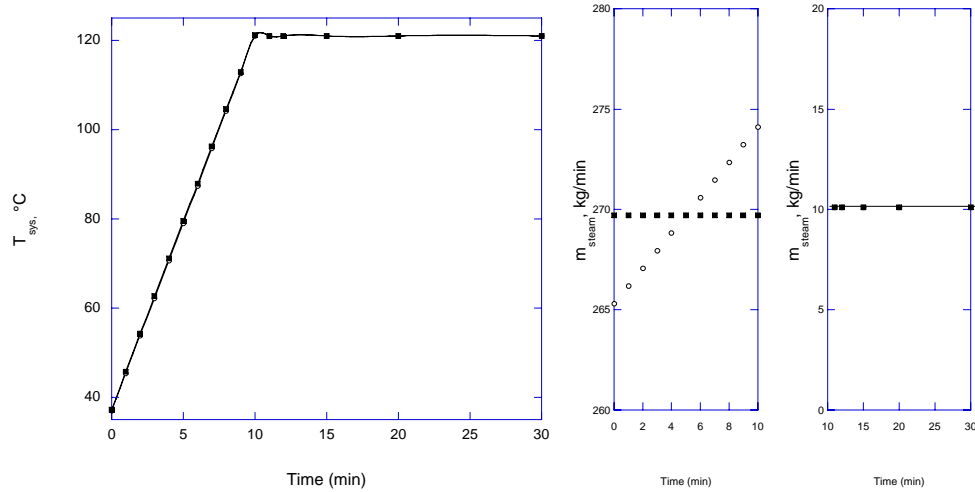
where C is a constant of integration. We find C and \dot{m}_{steam} by using the initial condition $T_{sys} = 37^\circ\text{C}$ at $t = 0$ and the final condition $T_{sys} = 121^\circ\text{C}$ at $t = 10 \text{ min}$:

$$C = -2557$$

$$\dot{m}_{steam} = 269.7 \text{ kg/min}$$

The total steam required during the warmup 10-min period is 2700 kg, and for warmup + sterilization we require 2900 kg.

The temperature profiles and steam condensation rates for these two cases are plotted. The two results do not differ much because, although the heat loss increases with time, the heat loss is small (about 4%) of the total heat required to increase the temperature.



For the case with linear temperature profile, the steam flow rate increases steadily as the heat loss increases. After 10 minutes, the steam requirement drops to 10.1 kg/min for both cases.

P6.67

The energy balance over the 12 hr time interval is

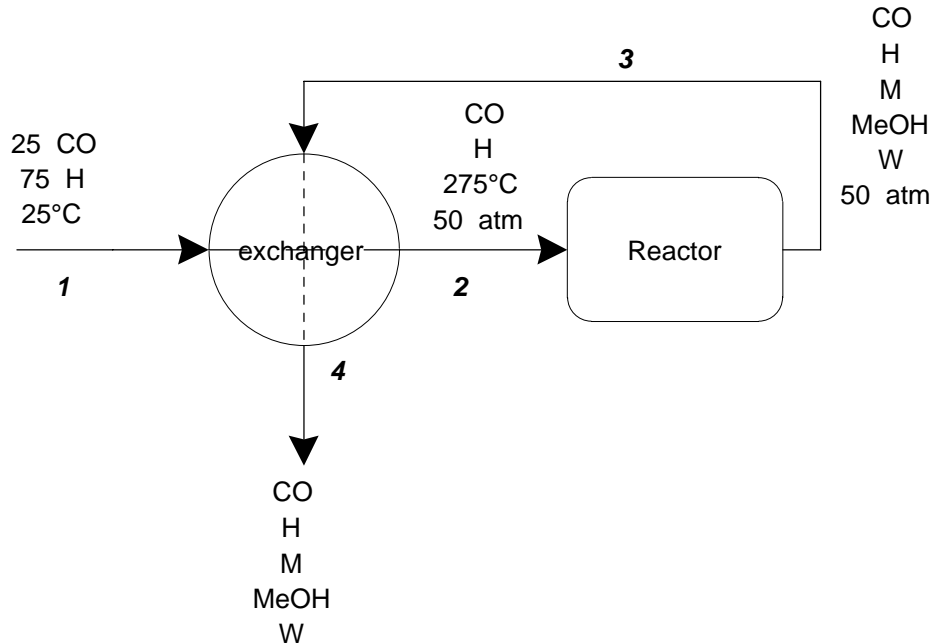
$$U_{sys,f} - U_{sys,0} = \int \dot{Q} dt$$

$$m_{drug} C_v (T_f - T_0) = 8000(2)(T_f - T_0) = \int_0^{12} 2.4 \times 10^5 \sin\left(\frac{\pi t}{24}\right) \cos\left(\frac{\pi t}{24}\right) dt$$

If we numerically evaluate the integral on the right hand side, we get 9.167×10^5 kJ. Inserting this into the energy balance, we find $T_f - T_0 = 57.3^\circ\text{C}$ or 103°F . Given the initial value of 50°F , the inside of the truck has reached 153°F after 12 h, above the allowable 140°F . To determine if the truck was at or above 140°F for 3 or more hours, we integrate from 0 to 9 hr. We find that the temperature in the truck reached 138°F after 9 hr, so we are just below the limit where we need to throw the drugs away.

P6.68

The labeled flow diagram for the part of the process of interest is



First we complete process flow calculations on the reactor. Flows are all in gmol/s.

$$\dot{n}_{CO,2} = 25$$

$$\dot{n}_{H,2} = 75$$

$$\dot{n}_{MeOH,3} = 18.7 = \dot{\xi}_1$$

$$\dot{n}_{CO,3} - \dot{n}_{CO,2} = 0.8 \times 25 = 20 = \dot{\xi}_1 + \dot{\xi}_2 = 18.7 + \dot{\xi}_2$$

$$\dot{\xi}_2 = 1.3$$

$$\dot{n}_{H,3} = 75 - 2(18.7) - 3(1.3) = 33.7$$

$$\dot{n}_{M,3} = \dot{\xi}_2 = 1.3$$

$$\dot{n}_{W,3} = \dot{\xi}_2 = 1.3$$

Flows in stream 4 equal those in stream 3.

Now we turn to the energy balance. The reactor is adiabatic and operates at steady state, and there is no work term. The differential energy balance reduces to:

$$\dot{H}_2 = \dot{H}_3$$

To calculate the difference in enthalpy between streams 2 and 3, we construct a path:

- decrease pressure of stream 2 from 50 atm to 1 atm
- decrease temperature of stream 2 from 275°C to 25°C
- react stream 2 to stream 3 through reactions R1 and R2 at 25°C
- increase temperature of stream 3 from 25°C to Tout
- increase pressure of stream 3 from 1 atm to 50 atm

The enthalpy change associated with change in pressure is negligible (steps (a) and (e)). (We are also neglecting any change in enthalpy due to mixing.) For the remaining calculations, we collect the following data (all compounds in vapor phase):

$$C_{p,CO} = 30.87 - 0.01285T + 2.789 \times 10^{-5}T^2 - 1.272 \times 10^{-8}T^3$$

$$C_{p,H} = 27.14 + 0.0093T - 1.381 \times 10^{-5}T^2 + 7.645 \times 10^{-9}T^3$$

$$C_{p,MeOH} = 21.15 + 0.07092T + 2.587 \times 10^{-5}T^2 - 2.852 \times 10^{-8}T^3$$

$$C_{p,M} = 19.25 + 0.05213T + 1.197 \times 10^{-5}T^2 - 1.132 \times 10^{-8}T^3$$

$$C_{p,W} = 32.24 - 0.001924T + 1.055 \times 10^{-5}T^2 - 3.596 \times 10^{-9}T^3$$

$$\Delta \hat{H}_{r1}^{\circ} = (-1)(-110.53) + (-2)(0) + (1)(-200.94) = -90.41 \text{ kJ/gmol}$$

$$\Delta \hat{H}_{r2}^{\circ} = (-1)(-110.53) + (-3)(0) + (1)(-74.52) + (1)(-241.83) = -205.82 \text{ kJ/gmol}$$

Both reactions are exothermic, which makes sense given that the reactor effluent is used to heat the reactants fed to the reactor.

$$\dot{H}_3 - \dot{H}_2 = \sum_i \dot{n}_{i2} \int_{275}^{T_3} C_{p,i} dT + \sum_k \dot{\xi}_k \Delta \hat{H}_{rk}^{\circ} + \sum_i \dot{n}_{i3} \int_{25}^{T_3} C_{p,i} dT = 0$$

We know everything but T_3 so can solve for the reactor effluent temperature (using Solver on a spreadsheet):

$$T_3 = 1300 \text{ K} \cong 1020^{\circ}\text{C}$$

The temperature of the product stream leaving the exchanger can be calculated either by choosing the exchanger as the system, or the exchanger plus reactor. We'll use just the exchanger. Assuming the heat exchanger is well-insulated, the steady state energy balance simplifies to:

$$\dot{H}_2 - \dot{H}_1 = \dot{H}_3 - \dot{H}_4$$

The only change in enthalpy occurs due to a change in temperature, so the energy balance equation simplifies further to:

$$\sum_i n_{i2} \int_{25}^{275} C_{pi} dT = \sum_i n_{i3} \int_{T_4}^{1000} C_{pi} dT$$

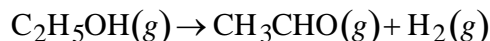
We find the product outlet temperature that satisfies this equation:

$$T_3 = 1060 \text{ K} \cong 790^{\circ}\text{C}$$

The temperature of the reactor effluent drops by 230°C. This is reasonable, since the reactant stream increased by about the same amount - 250°C – by heat exchange with the effluent.

P6.69

(a) The reaction is



To determine enthalpy of reaction at 300°C, we

(1) cool ethanol from 300°C to 25°C (using $C_p(g) = 65.5 \text{ J/gmol } ^\circ\text{C}$):

$$65.5(25 - 300) = -18,012 \text{ J/gmol} = -18.012 \text{ kJ/gmol}$$

(2) react at 25°C (using gas phase enthalpy of formation):

$$\Delta \hat{H}_r^\circ = \sum_i \nu_i \Delta \hat{H}_{f,i}^\circ = (-1)(-234.95) + (-166.2) + 0 = +68.75 \text{ kJ/gmol}$$

(3) heat products from 25°C to 300°C (using $C_p(g) = 54.7$ for acetaldehyde and 29.1 for hydrogen):

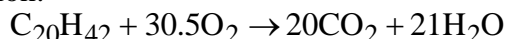
$$(54.7 + 29.1)(25 - 300) = 23,045 \text{ J/gmol} = +23.045 \text{ kJ/gmol}$$

Therefore $\Delta \hat{H}_r(300^\circ\text{C}) = -18.012 + 68.75 + 23.045 = +73.8 \text{ kJ/gmol}$ ethanol reacted. (We neglect any pressure correction since this is all in the gas phase.)

(b) The reaction is highly endothermic, so the process will not work as sketched. Heat input is required to maintain the reactor temperature. The reactants must be heated much hotter than 300°C in the preheater (the temperature in the reactor will decrease to a minimum of 300°C as the reaction proceeds), in which case the reactor products are cooler than the reactor feed and so cannot be used to supply the heat.

P6.70

(a) We have the enthalpy of reaction for combustion, and can relate that to enthalpy of formation:

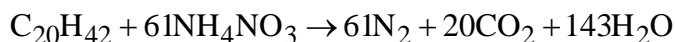


$$\Delta \hat{H}_r^\circ = -12390 \text{ kJ/gmol} = \sum_i \nu_i \Delta \hat{H}_{f,i}^\circ = (-1)\Delta \hat{H}_{f,E}^\circ + 20(-393.5) + 21(-241.8)$$

$$\Delta \hat{H}_{f,E}^\circ = -558.4 \text{ kJ/gmol}$$

(b) 4880 g $\text{NH}_4\text{NO}_3 = 61 \text{ gmol}$. 282 g eicosane = 1 gmol.

The balanced chemical reaction is



$$\Delta \hat{H}_r^\circ = \sum_i \nu_i \Delta \hat{H}_{f,i}^\circ = (-1)(-558.4) + (-61)(-365) + 20(-393.5) + 143(-241.8)$$

$$\Delta \hat{H}_r^\circ = -19,624 \text{ kJ/gmol eicosane}$$

or, -321.7 kJ/gmol ammonium nitrate.

(c) Assuming the 2000 kg ammonium nitrate was spiked with eicosane at the same ratio as part (b), then this is equivalent to 25000 gmol ammonium nitrate plus 410 gmol eicosane reacted in one second, or

$$\frac{19625 \text{ kJ}}{\text{gmol}} \times \frac{410 \text{ gmol}}{\text{s}} \times \frac{\text{hp}}{0.7457 \text{ kJ/s}} = 10.8 \text{ million hp!!}$$

P6.71

The surface area of the pilot scale reactor is (cylinder area plus two ends)

$$A = \pi(2.5)(100) + 2 \frac{\pi(2.5)^2}{4} = 795 \text{ cm}^2$$

Therefore, the heat loss from the pilot-scale reactor is $3.8(795) = 3021 \text{ W} = 3021 \text{ J/s}$. Given the enthalpy of reaction, and assuming that it is independent of temperature, since this rate of heat loss is just enough to match the enthalpy change due to reaction,

$$\dot{\xi} = \frac{-3021 \text{ J/s}}{-2000 \text{ J/g}} = 1.5 \text{ g/s}$$

Now we scale up to 1000-fold larger-volume production rate, so $\dot{\xi} = 1500 \text{ g/s}$. We increase the volume in the reactor by 1000-fold, or, since the length remains constant, the diameter increases by 10-fold, to 25 cm. The surface area of the larger reactor is

$$\pi(25)(100) + 2 \frac{\pi(25)^2}{4} = 8835 \text{ cm}^2$$

so the heat loss through the reactor walls is $3.8(8835) = 33573 \text{ J/s}$. But, the enthalpy change due to reaction is $(-2000)(1500) = -3,000,000 \text{ J/s}$. This means that the process stream must heat up. If we estimate the heat capacity as $2 \text{ J/g } ^\circ\text{C}$ (per our rule of thumb), then by an energy balance:

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

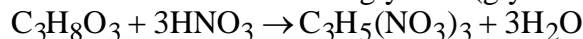
$$-3,000,000 \text{ J/s} + 1500 \text{ g/s} (2 \text{ J/g } ^\circ\text{C})(T_{out} - T_{in}) = -33,573 \text{ J/s}$$

$$T_{out} - T_{in} = 989^\circ\text{C!!}$$

Although heat removal is not an issue with the small pilot-scale reactor, it is of enormous importance when we scale up!

P6.72

(a) The balanced reaction between glycerol (glycerin) and nitric acid is

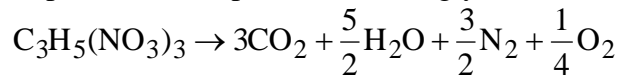


The standard enthalpy of reaction for liquid-phase reactants and products is

$$\Delta \hat{H}_r^\circ = \sum_i \nu_i \Delta \hat{H}_{f,i}^\circ = (-1)(-665.9) + (-3)(-173.22) + (1)(-371.1) + (3)(-285.84) = -44 \text{ kJ/gmol}$$

The reaction is slightly exothermic.

(b) The explosive decomposition of nitroglycerin is



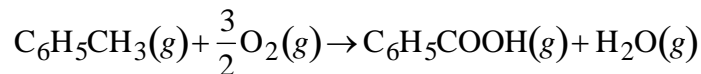
with

$$\Delta \hat{H}_r^\circ = \sum_i \nu_i \Delta \hat{H}_{f,i}^\circ = (-1)(-371.1) + (3)(-393.5) + \left(\frac{5}{2}\right)(-285.84) = -1524 \text{ kJ/gmol}$$

Very exothermic!

P6.73

(a) The reaction is:



Since it is a partial oxidation reaction, the reaction is likely exothermic, and the enthalpy of reaction is likely negative.

We need some data:

Toluene: $\Delta \hat{H}_f^\circ = 50.17 \text{ kJ/gmol}$ (vapor)

$C_p = 103.8 \text{ J/gmol } ^\circ\text{C}$ (vapor)

At $T_b = 110.6^\circ\text{C}$, $\Delta \hat{H}_v = 33.2 \text{ kJ/gmol}$

Benzoic acid: $\Delta \hat{H}_f^\circ = -385.2 \text{ kJ/gmol}$ (solid)

$C_p = 20.06 + 0.28T(\text{K}) \text{ J/gmol } ^\circ\text{C}$ (vapor)

At $T = 25^\circ\text{C}$, $\Delta \hat{H}_{sub} = 89 \text{ kJ/gmol}$ (sublimation enthalpy change)

(Data found in Lange's Handbook of Chemistry and NIST Chemistry Webbook)

Oxygen: $\Delta \hat{H}_f^\circ = 0 \text{ kJ/gmol}$ (gas)

$C_p = 29.1 \text{ J/gmol } ^\circ\text{C}$ (vapor)

Water: $\Delta \hat{H}_f^\circ = -241.43 \text{ kJ/gmol}$ (vapor)

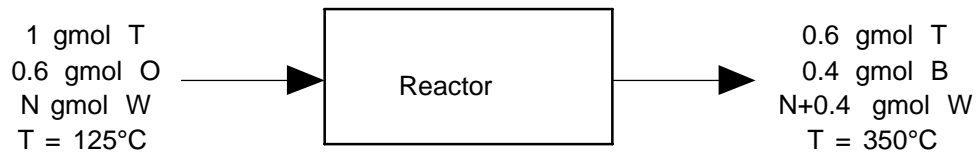
$\Delta \hat{H}_v = 44.01 \text{ kJ/gmol}$ (25°C)

$C_p = 32.24 + 0.001924T + 1.055e-5T^2 - 3.596e-9T^3 \text{ J/gmol } ^\circ\text{C}$ (vapor)

The enthalpy of reaction in the gas phase is:

$$\Delta \hat{H}_r^\circ = (-1)(50.17) + (1)(-385.2 + 89) + (1)(-241.83) = -588.2 \text{ kJ/gmol}$$

(b) The reactor as the system and the basis is 1 gmol/s toluene (T) fed, with O for oxygen, W for H₂O, and B for benzoic acid. From the reactor performance specification, we know that all the oxygen is consumed, and from the reaction stoichiometry we know that 0.4 gmol toluene is consumed, and 0.4 gmol benzoic acid plus 0.4 gmol water is generated, per 0.6 gmol oxygen consumed. From the material balance, the flow diagram is:



The energy balance simplifies to $\dot{H}_{in} - \dot{H}_{out} = 0$. We'll calculate the change in enthalpy as:

(1) Cool reactor inlet from 125°C to 25°C (in the vapor phase):

$$\begin{aligned} & 1(103.8)(25 - 125) + 0.6(29.1)(25 - 125) + n \int_{398K}^{298K} C_p dT \\ & = -10,380 + (-1746) + (-3404n) = -12126 - 3404n \text{ J/s} \end{aligned}$$

where n = the molar flow rate of steam into the reactor.

(2) react 0.4 gmol toluene at 25°C in the gas phase

$$-588.2(0.4)(1000) = -235,380 \text{ J/s}$$

(3) heat reactor outlet from 25°C to 350°C in the gas phase

$$\begin{aligned} & 0.4(103.8)(350 - 25) + 0.4 \int_{298K}^{623K} C_{p,B} dT + (n + 0.4) \int_{298K}^{623K} C_{p,W} dT \\ & = 13,494 + 19,370 + (n + 0.4)11,395 = 37422 + 11395n \text{ J/s} \end{aligned}$$

The enthalpy change must sum to zero to satisfy the energy balance:

$$-12126 - 3404n - 235,380 + 37422 + 11395n = -210,084 + 7991n = 0$$

$$n = 26.3 \text{ gmol/s}$$

Over 26 gmol steam are required per gmol toluene fed to control the reactor temperature in this highly exothermic reaction.

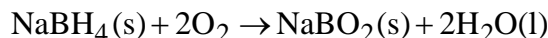
P6.74

From the Knovel website or the NIST Chemistry webbook, we find enthalpy of formation data for sodium borohydride and sodium metaborate:

$$\Delta \hat{H}_f^\circ = -191.84 \text{ kJ/gmol for NaBH}_4 \text{ (solid)}$$

$$\Delta \hat{H}_f^\circ = -975.71 \text{ kJ/gmol for NaBO}_2 \text{ (solid) (and } -960.02 \text{ for the liquid)}$$

Data for enthalpy of solution of sodium borohydride and sodium metaborate was not available. We calculate the overall enthalpy of the reaction



$$\Delta \hat{H}_r^\circ = (-1)(-191.84) + (1)(-975.71) + (2)(-285.84) = -1355.55 \text{ kJ/gmol}$$

or, since the molar mass of NaBH₄ is 38 g/gmol, $\Delta \hat{H}_r^\circ = -35.7 \text{ kJ/g}$.

At 33% conversion to electrical energy, this is about 12 kJ electrical work generated per g NaBH₄.

One of the interesting factors with this system is that the mass of the battery increases with reaction, since the oxygen in the air reacts with the fuel to make two condensed products. The increase is significant: a fuel cell containing 100 g NaBH₄ will increase to 268 g (173 g NaBO₂ plus 95 g water). If you can just throw the used canister away, then the portability is good because you avoid having to carry around the oxidant in the fuel cell.

Alternative technology using similar reaction chemistry is being developed: sodium borohydride reacts with water to make hydrogen and sodium metaborate; the hydrogen is then used in a fuel cell, where it reacts with oxygen to make water and energy is released.

P6.75

(a) The energy balance around the reactor is:

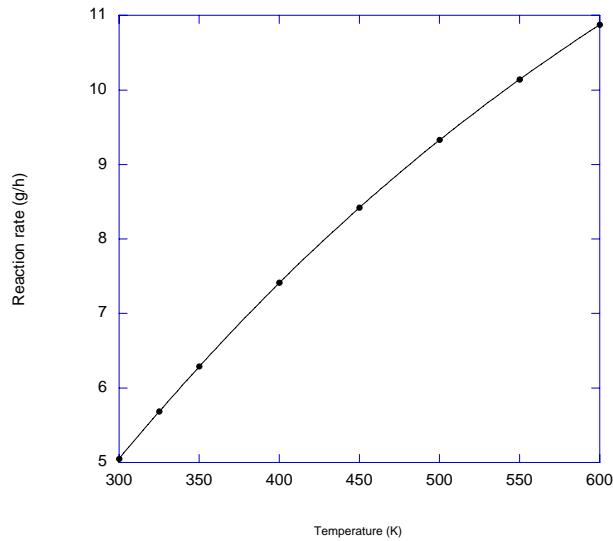
$$\dot{H}_{out} - \dot{H}_{in} = \dot{Q}$$

Since the reactor operates at 298K, and the reactants enter and leave at this temperature:

$$\dot{H}_{out} - \dot{H}_{in} = \dot{R} \Delta \hat{H}_r^\circ = (-4.2 \text{ kJ/g}) \dot{R}$$

From the problem statement, $\dot{Q} = -21 \text{ kJ/h}$, therefore, $\dot{R} = \frac{-21}{-4.2} = 5 \text{ g/h}$

(b) The reaction rate as a function of temperature is plotted below, with $\dot{R}_{298} = 5 \text{ g/h}$



(c) Once the cooling is turned off, the energy balance changes to:

$$\dot{H}_{out} - \dot{H}_{in} = 0$$

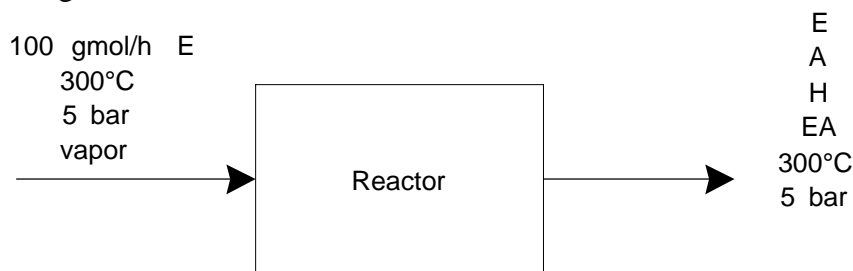
Choosing the reactor inlet fluid at 298 K as the reference state, $\dot{H}_{in} = 0$. To calculate \dot{H}_{out} , (we assume the enthalpy of reaction is independent of temperature):

$$\begin{aligned} \dot{H}_{out} &= \dot{R}\Delta H_r^\circ + \dot{m}C_p(T - 298) \\ \dot{H}_{out} = 0 &= 5 \exp\left(460\left(\frac{1}{298} - \frac{1}{T}\right)\right)(-4200) + 52(4)(T - 298) \\ T &= 478K \end{aligned}$$

Kaboom!

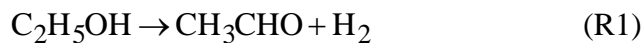
P6.76

The flow diagram is



where the components are ethanol E, acetaldehyde A, hydrogen H and ethyl acetate EA.

The two reactions are



By material balance and the specifications given:

$$\dot{n}_{E,out} = 100 - \dot{\zeta}_1 - 2\dot{\zeta}_2 = 0.10(100) = 10$$

$$\dot{\zeta}_1 + 2\dot{\zeta}_2 = 90 \text{ gmol/h}$$

$$y_{E \rightarrow A} = 0.65 = \frac{\dot{\zeta}_1}{\dot{\zeta}_1 + 2\dot{\zeta}_2} = \frac{\dot{\zeta}_1}{90}$$

$$\dot{\zeta}_1 = 58.5 \text{ gmol/h}$$

$$\dot{\zeta}_2 = 15.75 \text{ gmol/h}$$

$$\dot{n}_{A,out} = \dot{\zeta}_1 = 58.5 \text{ gmol/h}$$

$$\dot{n}_{H,out} = \dot{\zeta}_1 + 2\dot{\zeta}_2 = 90 \text{ gmol/h}$$

$$\dot{n}_{EA,out} = \dot{\zeta}_2 = 15.75 \text{ gmol/h}$$

The energy balance simplifies to

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

To calculate the enthalpy change from in to out, we construct a pathway:

- (a) cool 100 gmol/h ethanol vapor from 300°C to 25°C (573 K to 298 K)
- (b) decrease pressure of ethanol vapor from 5 bar to 1 bar
- (b) react via R1 and R2 at the calculated extents of reaction, in the vapor phase at 25°C and 1 bar
- (d) increase pressure of reaction mix from 1 bar to 5 bar, at 25°C and in vapor phase
- (e) increase temperature of products from 25°C to 300°C.

Assuming ideal gas behavior, there is no change in enthalpy with change in pressure. For the remainder, we find physical property data in Appendix B.

$$\Delta \hat{H}_{r1}^\circ = (-1)(-234.95) + (1)(-166.2) = +68.75 \text{ kJ/gmol}$$

$$\Delta \hat{H}_{r2}^\circ = (-2)(-234.95) + (1)(-444.5) = +25.4 \text{ kJ/gmol}$$

$$C_{p,E} = 65.5 \text{ J/gmol } ^\circ\text{C}$$

$$C_{p,A} = 54.7 \text{ J/gmol } ^\circ\text{C}$$

$$C_{p,H} = 29.1 \text{ J/gmol } ^\circ\text{C}$$

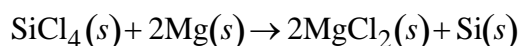
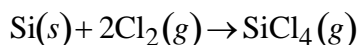
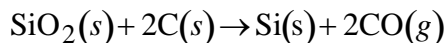
$$C_{p,EA} = 113.6 \text{ J/gmol } ^\circ\text{C}$$

with all heat capacities the approximate values for the vapor-phase compounds. Then

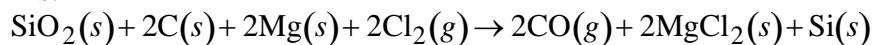
$$\begin{aligned}\dot{Q} &= \dot{H}_{out} - \dot{H}_{in} = 100(65.6)(298 - 573) + 58.5(68,750) + 15.75(25,400) \\ &\quad + [10(65.6) + 58.5(54.7) + 90(29.1) + 15.75(113.6)](573 - 298) \\ \dot{Q} &= 4,890,566 \text{ J/h} = 4,891 \text{ kJ/h}\end{aligned}$$

Heat must be added to the reactor to maintain the temperature, which makes sense because both reactions are endothermic.

P6.77



Net reaction is:



In table form:

Compound	v_i	M_i	$v \quad M_i$
SiO ₂	-1	60	-60
C	-2	12	-24
Mg	-2	24	-48
Cl ₂	-2	71	-142
CO	2	28	56
Si	1	28	28
MgCl ₂	2	95	190

Or, per gram of Si (obtained by dividing all numbers in the last column by 28), we require 2.14 g SiO₂, 0.86 g C, 1.71 g Mg, and 5.07 g Cl₂. Byproducts are 2 g CO and 6.79 g MgCl₂.

Using $\Delta\hat{H}_f^\circ$ data from App. B for SiO₂, CO, and MgCl₂ (for all others, $\Delta\hat{H}_f^\circ = 0$), we calculate

$$\Delta\hat{H}_r^\circ = 2(-110.53) + 2(-641.1) + (-1)(-850.8) = -652.5 \text{ kJ/gmol}$$

or, per gram of Si

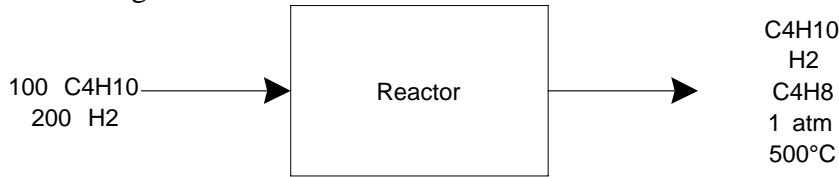
$$\Delta\hat{H}_r^\circ = \frac{-652.5 \text{ kJ/gmol}}{28 \text{ g/gmol}} = -23.3 \text{ kJ/g}$$

23.3 kJ must be removed per gram Si.

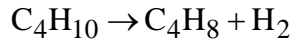
P6.78

This problem reviews material from Chapter 4 along with covering some material on energy balances.

The flow diagram is



where we choose as a basis 300 gmol/h fed to the reactor. The balanced chemical reaction is



From material balances;

$$\dot{m}_{\text{C}_4\text{H}_{10},out} = 100 - \xi$$

$$\dot{m}_{\text{C}_4\text{H}_8,out} = \xi$$

$$\dot{m}_{\text{H}_2,out} = 200 + \xi$$

From the equilibrium constant:

$$K_a = 0.1216 \text{ atm} = \frac{y_{\text{C}_4\text{H}_8} y_{\text{H}_2}}{y_{\text{C}_4\text{H}_{10}}} P = \frac{\left(\frac{\xi}{300}\right)(200 + \xi)}{(100 - \xi)(300 + \xi)} (1 \text{ atm})$$

The solution is;

$$\xi = 15.1$$

therefore

$$\dot{m}_{\text{C}_4\text{H}_{10},out} = 84.9$$

$$\dot{m}_{\text{C}_4\text{H}_8,out} = 15.1$$

$$\dot{m}_{\text{H}_2,out} = 215.1$$

The reactor is adiabatic, at steady state, and without a work term. Therefore, the energy balance becomes simply;

$$\dot{H}_{out} - \dot{H}_{in} = 0$$

The enthalpy of reaction at 500°C (773 K) is given: $\Delta \hat{H}_r = +139.5 \text{ kJ/gmol}$. We know the conditions at the outlet but not at the inlet. We construct an enthalpy path from inlet to outlet:

- change reactants from T_{in} to 500 °C (773 K)
- react at 773 K to equilibrium

The energy balance equation becomes;

$$\dot{H}_{out} - \dot{H}_{in} = 0 = 200 \int_{T_{in}}^{773} C_{p,\text{C}_4\text{H}_{10},v} dT + 100 \int_{T_{in}}^{773} C_{p,\text{H}_2} dT + 15.1(139,500)$$

Heat capacity data is obtained from Table B.17;

$$C_{p,C_4H_{10},v} = -1.390 + 0.3847T - 1.846 \times 10^{-4}T^2 + 2.895 \times 10^{-8}T^3$$

$$C_{p,C_4H_8,v} = 16.05 + 0.2804T - 1.091 \times 10^{-4}T^2 + 9.098 \times 10^{-9}T^3$$

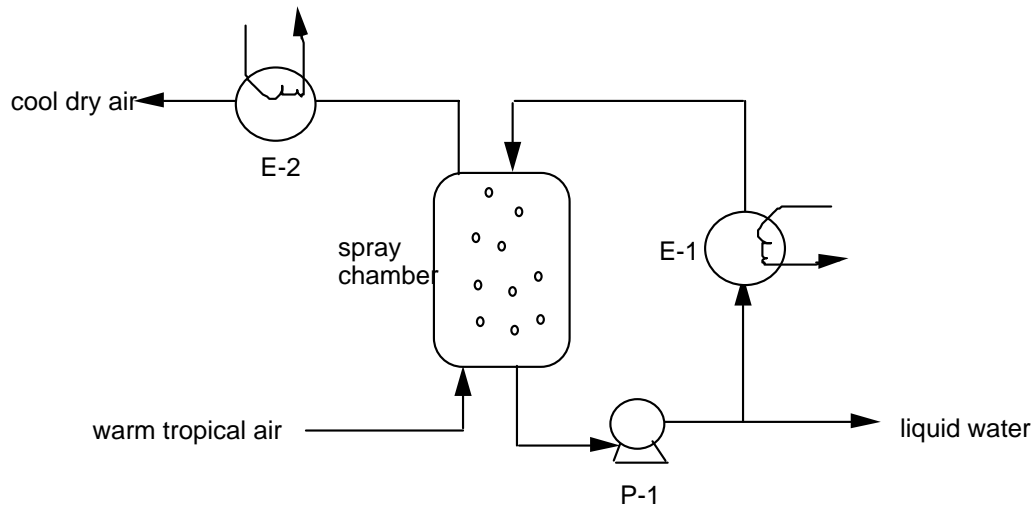
$$C_{p,H_2,v} = 27.14 + 0.0093T - 1.381 \times 10^{-5}T^2 + 7.645 \times 10^{-9}T^3$$

We substitute in these expressions into the energy balance equation and solve to find:

$$T = 871 \text{ K} = 598^\circ\text{C}.$$

The temperature should be higher at the inlet because the reaction is endothermic.

P6.79



(a) Since the spray chamber acts as a single equilibrium stage, the cool air leaving the spray chamber is equilibrated with liquid water at 45°F . This means the air is at 45°F (7.2°C) and is saturated with water vapor. To calculate the mole fraction of water vapor in the air, we use Raoult's Law, and Antoine's equation to estimate the saturation pressure.

$$\log P_w^{sat} = 8.10765 - \frac{1750.286}{235 + 7.2} = 0.881$$

or $P_w^{sat} = 7.6 \text{ mmHg}$ at 45°F , and

$$y_w = \frac{x_w P_w^{sat}}{P} = \frac{P_w^{sat}}{P} = \frac{7.6}{760} = 0.01$$

Since there is 1000 gmol/h cool air + water vapor leaving the spray chamber, there must be $10 \text{ gmol/h H}_2\text{O}$ and 990 gmol/h air .

The dewpoint of the incoming warm air is 90°F (32.2°C), at which $P_w^{sat} = 36$ mmHg (from Antoine equation). Thus, $y_w = 0.048$, and the incoming air contains 50 gmol/h water vapor along with the 990 gmol/h air. (We use the dewpoint, not the actual, temperature, to calculate the water content.) Therefore, the water removed from the air in the spray chamber is 50-10 or 40 gmol/h.

(b) Air leaving the spray chamber is at 45°F. E-2 would actually warm the air up! The temperature rises from 45°F to 68°F (20°C). Using $C_p = 29$ J/gmol °C for air and 33.6 J/gmol °C for water vapor,

$$\dot{Q} = [990(29) + 10(33.6)](20 - 7.2) = +3.72 \times 10^5 \text{ J/h}$$

E-1 removes heat. If we consider the spray chamber, P-1 and E-1 together as the system, the energy balance is:

$$\dot{Q} + \dot{W}_s = \dot{H}_{out} - \dot{H}_{in}$$

We'll neglect the work input at the pump P-1. The enthalpy change includes (1) cooling 990 gmol/h dry air from 95°F to 45°F, (2) cooling 50 gmol/h water vapor from 95°F to 45°F, and (3) condensing 40 gmol/h water. We'll calculate this as:

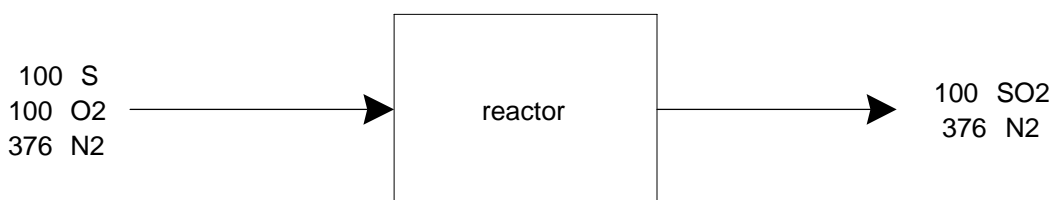
$$\dot{Q} = \dot{H}_{out} - \dot{H}_{in} = 990(29)(7.2 - 35) + 50(33)(7.2 - 35) + 40(-44,000) = -2.60 \times 10^6 \text{ J/h}$$

Nearly 70% of the duty is required for water condensation.

(c) no, 60°F water isn't cold enough to cool and condense water to 45°F.

P6.80

For the case where air is fed in stoichiometric quantities, at an arbitrary basis of 100 gmol/s, assuming air is 79 mol% N₂ and 21 mol% O₂:



If the reactor is adiabatic and steady state, the energy balance simplifies to:

$$0 = \dot{H}_{out} - \dot{H}_{in}$$

If the reactants are fed at 25°C, we envision a path for enthalpy calculations:

- (a) react 100 gmol/s S and O₂ to SO₂ at 298 K
- (b) heat SO₂ and N₂ to T_{out} .

From Table B.3

$$\Delta\hat{H}_r^\circ = \Delta\hat{H}_f^\circ, \text{SO}_2 = -296.81 \text{ kJ/gmol}$$

From Table B.17

$$C_{p,N_2} = 31.15 - 0.01357T + 2.680 \times 10^{-5}T^2 - 1.168 \times 10^{-8}T^3$$

$$C_{p,\text{SO}_2} = 23.85 + 0.06699T - 4.9610 \times 10^{-5}T^2 + 1.328 \times 10^{-8}T^3$$

in units of J/gmol K.

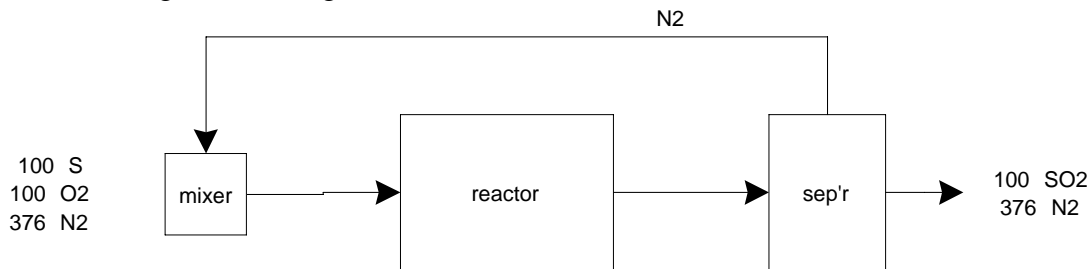
The energy balance equation becomes

$$0 = \dot{H}_{out} - \dot{H}_{in} = 100(-296,810) + 376 \int_{298}^{T_{out}} C_{p,N_2} dT + 100 \int_{298}^{T_{out}} C_{p,\text{SO}_2} dT$$

where heat capacities are given above. Solving using GOALSEEK on EXCEL, we find
 $T_{out} = 2100 \text{ K} \approx 1800^\circ\text{C}$

which is way above the allowable 450°C .

(a) The flow diagram is changed to:



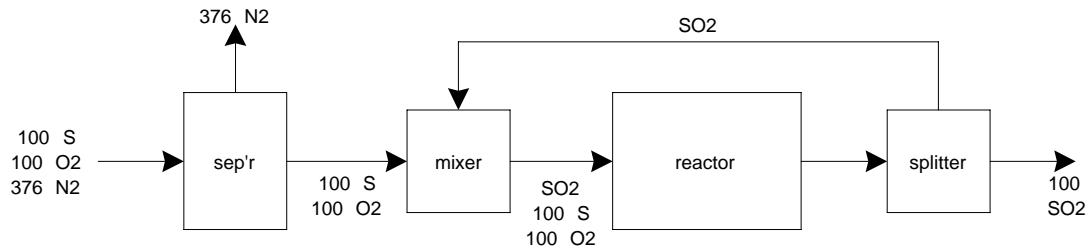
What we want to find is the flow rate of nitrogen recycle N_R required to maintain the reactor outlet temperature at 450°C (723 K). We'll design so that we cool the recycled nitrogen stream to 25°C . The energy balance changes slightly:

$$0 = \dot{H}_{out} - \dot{H}_{in} = 100(-296,810) + (N_R + 376) \int_{298}^{723} C_{p,N_2} dT + 100 \int_{298}^{723} C_{p,\text{SO}_2} dT$$

Solving we find

$$N_R = 1800 \text{ gmol/s}$$

(b) Now the flow diagram is:



Assuming the SO_2 is cooled to 25°C before recycling back to the mixer, the energy balance changes to:

$$0 = \dot{H}_{out} - \dot{H}_{in} = 100(-296,810) + (100 + S_R) \int_{298}^{723} C_{p,\text{SO}_2} dT$$

where S_R = the flow rate of recycled SO_2 .

Solving, we find

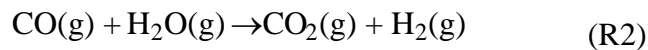
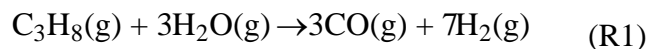
$$S_R = 1400 \text{ gmol/s}$$

Although the gas flow rate through the reactor (in gmol/s) is lower in option (b), this option has some significant drawbacks. Chief among them is the expense of separating N_2 from O_2 , which is more expensive than separating N_2 from SO_2 . Also, option (a) decouples the flow rate of cooling gas from the production of SO_2 by chemical reaction.

We could replace the separator of option (a) with a splitter, which is cheaper.

P6.81

(a) With the two reactions



The steady-state material balances (in units of gmol/s) around the reactor are:

$$\begin{array}{lll} \text{C}_3\text{H}_8: & 10 - \xi_1 = 0 & \text{so } \xi_1 = 10 \\ \text{H}_2\text{O}: & 60 - 3\xi_1 - \xi_2 = 30 - \xi_2 = \dot{n}_{\text{H}_2\text{O},out} \\ \text{CO}: & 3\xi_1 - \xi_2 = 30 - \xi_2 = \dot{n}_{\text{CO},out} \\ \text{H}_2: & 7\xi_1 + \xi_2 = 70 + \xi_2 = \dot{n}_{\text{H}_2,out} \\ \text{CO}_2: & \xi_2 = \dot{n}_{\text{CO}_2,out} \end{array}$$

The heating gas supplies heat to the reactor:

$$\dot{Q} = (360 \text{ gmol/s})(0.04 \text{ kJ/gmol} \cdot \text{s})(1400 - 900^\circ\text{C}) = 7200 \text{ kJ/s}$$

The steady-state energy balance around the reactor simplifies to:

$$\dot{Q} = 7200 \text{ kJ/s} = \dot{H}_{out} - \dot{H}_{in}$$

To calculate $\dot{H}_{out} - \dot{H}_{in}$:

(1) cool reactants (propane and hydrogen) from 125 to 25°C (398 to 298 K) (use C_p values in App. B)

$$\sum \dot{n}_i \int_{T_{in}}^{T_{ref}} C_{p,i} dT = (10) \int_{398}^{298} C_{p,C_3H_8} dT + (60) \int_{398}^{298} C_{p,H_2} dT = -84.4 - 204 \text{ kJ/s}$$

(2) react at 298 K, with

$$\Delta \hat{H}_{R1}^\circ = (3)(-110.53) + (-1)(-104.68) + (-3)(-241.83) = 498.6 \text{ kJ/gmol}$$

$$\Delta \hat{H}_{R2}^\circ = (1)(-391.6) + (-1)(-110.53) + (-1)(-241.83) = -39.2 \text{ kJ/gmol}$$

$$\sum \zeta_k \Delta \hat{H}_{r,k}^\circ = 10(498.6) + \xi_2(-39.2) = 4986 - 39.2\xi_2$$

(3) heat products from 25°C to 800°C (298 to 1073 K)

$$\begin{aligned} \sum \dot{n}_i \int_{T_{ref}}^{T_{out}} C_{p,i} dT &= (30 - \xi_2) \int_{298}^{1073} C_{p,H_2O} dT + (30 - \xi_2) \int_{298}^{1073} C_{p,CO} dT + (\xi_2) \int_{298}^{1073} C_{p,CO_2} dT + (70 + \xi_2) \int_{298}^{1073} C_{p,H_2} dT \\ &= 30.1(30 - \xi_2) + 24.1(30 - \xi_2) + 37.4\xi_2 + 22.9(70 + \xi_2) \end{aligned}$$

Therefore:

$$\begin{aligned} \dot{Q} = 7200 \text{ kJ/s} &= \dot{H}_{out} - \dot{H}_{in} = \\ &= -84.4 - 204 + 4986 - 39.2\dot{\xi}_2 + 903 - 30.1\dot{\xi}_2 + 723 - 24.1\dot{\xi}_2 + 37.4\dot{\xi}_2 + 1603 + 22.9\dot{\xi}_2 \end{aligned}$$

Solving, $\dot{\xi}_2 = 21.95 \text{ gmol/s}$

Now we use this value in the material balance equations and find that the reactor outlet stream flow rate is 102 gmol/s total, with 8 gmol/s H₂O, 8 gmol/s CO, 8 gmol/s CO₂, and 78 gmol/s H₂.

The heat exchanger must cool the product streams to 298 K and condense all the water.

The energy balance is:

$$\dot{Q} = \dot{H}_{out} - \dot{H}_{in} = \sum \dot{n}_i \int_{T_{out}}^{T_{in}} C_{p,i} dT + \dot{n}_{H_2O} (-\Delta \hat{H}_{vap}) = -2519 + 8(-44) = -2871 \text{ kJ/s}$$

The heat removal rate in the exchanger is less than the heat addition rate in the reactor, because the net reaction is endothermic.

(b) If the temperature of the heating gas leaving the reactor rises to 1000 °C, then

$$\dot{Q} = (360 \text{ gmol/s})(0.04 \text{ kJ/gmol} \cdot \text{s})(1400 - 1000^\circ\text{C}) = 5760 \text{ kJ/s}$$

The temperature of the reactor effluent stream also increases, to 900°C (1173 K). With less heat transfer into the reactor, but a higher exit temperature, then the endothermic reaction (R1) must no longer go to completion. Re-evaluating the energy balance with these new temperatures, we find:

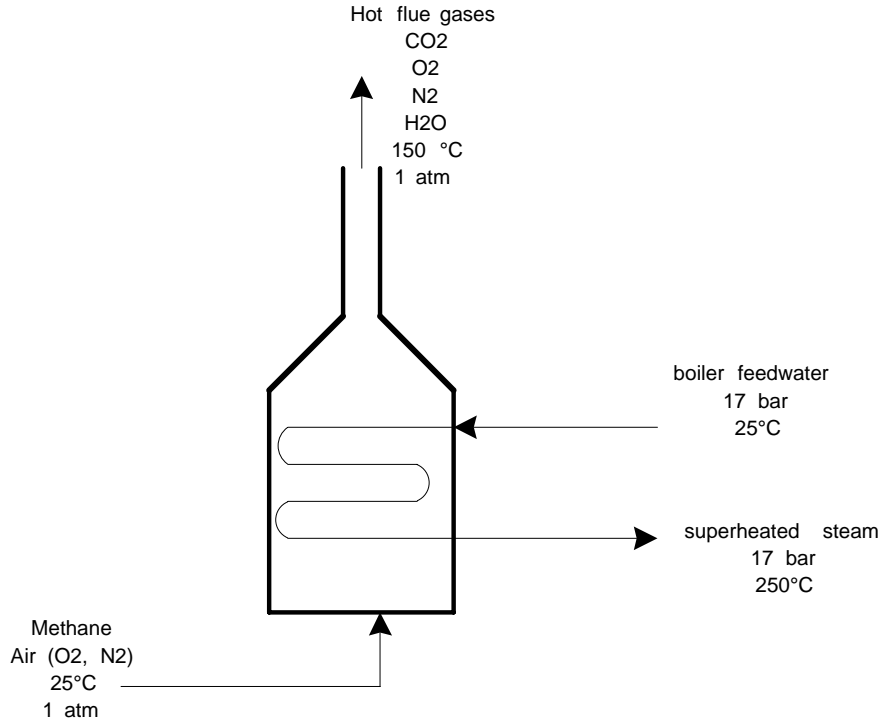
$$\begin{aligned} \dot{Q} = 5760 \text{ kJ/s} = \dot{H}_{out} - \dot{H}_{in} = & -84.4 - 204 + 498.6\dot{\xi}_1 - 39.2\dot{\xi}_2 \\ & + 124.6(10 - \dot{\xi}_1) + 33.3(60 - 3\dot{\xi}_1 - \dot{\xi}_2) + 27.2(3\dot{\xi}_1 - \dot{\xi}_2) + 42.2\dot{\xi}_2 + (7\dot{\xi}_1 + \dot{\xi}_2)25.8 \end{aligned}$$

There are an infinite number of solutions mathematically possible, but there are some constraints on a physically reasonable solution (in particular, avoiding negative flows). If we require that $\dot{\xi}_1 \leq 10$ and $3\dot{\xi}_1 - \dot{\xi}_2 \geq 0$, we find for example that $\dot{\xi}_1 = 6.35$ and $\dot{\xi}_2 = 19$ satisfies these constraints and the energy balance equation. The reactor outlet contains 3.65 gmol/s propane, 21.9 gmol/s water, 0 gmol/s CO, 63.45 gmol/s hydrogen, and 19 gmol/s CO₂. The rate of heat removal in the heat exchanger increases since the reactor outlet temperature is higher.

P6.82

(Note to instructor: consider trying a variant of this problem, where the boiler feed water enters as saturated liquid at 17 bar (204°C). An energy-efficient solution requires that some of the hot combustion gases be used in a countercurrent heat exchanger with incoming methane/air, in addition to the furnace.)

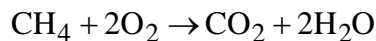
The boiler feed water enters the boiler at 25°C and, we'll assume, 17 bar, and leaves at 250°C as superheated steam. Methane and air enter the furnace at 25°C and are combusted; the hot combustion gases exchange heat with the steam and exit at 150°C. Flows in the furnace are set up so that the heat exchange is countercurrent; the cool feedwater is in contact with the cooler flue gases while the hot steam is in contact with the hot combustion gases near the burners.



From the NIST Chemistry Webbook, for water at 17 bar and 25°C, $\hat{H} = 106.4$ kJ/kg. For superheated steam at 17 bar and 250°C, $\hat{H} = 2915.8$ kJ/kg. At 12,100 kg/h, the energy balance with the water/steam in the furnace tubes as the system, simplifies to

$$\dot{Q} = \dot{H}_{out} - \dot{H}_{in} = \dot{m}_{steam} (\hat{H}_{out} - \hat{H}_{in}) = 12100(2915.8 - 106.4) = 33.99 \times 10^6 \text{ kJ/h.}$$

This is the heat flow that must be supplied from combustion of methane. The balanced chemical reaction is:



with all compounds in the vapor phase. We'll let $\dot{n}_{M,in}$ be the required molar flow rate of methane to the burner. Then, the oxygen flow to the burner is $\dot{n}_{O,in} = 2.4\dot{n}_{M,in}$ since it is fed at 20% above the stoichiometric requirement. The nitrogen flow is $\dot{n}_{N,in} = 3.76\dot{n}_{O,in} = 9.024\dot{n}_{M,in}$. From material balances, we find $\dot{n}_{O,out} = 0.4\dot{n}_{M,in}$, $\dot{n}_{N,out} = \dot{n}_{N,in} = 9.024\dot{n}_{M,in}$, $\dot{n}_{C,out} = \dot{n}_{M,in}$, and $\dot{n}_{W,out} = 2\dot{n}_{M,in}$, where C and W are carbon dioxide and water, respectively, leaving in the flue gas. The data required is:

$$\Delta\hat{H}_{c,CH_4}^\circ = -802.6 \text{ kJ/gmol}$$

with water vapor as the product of combustion and

$$C_{p,CO_2} = 37.0 \text{ J/gmol } ^\circ\text{C}$$

$$C_{p,H_2O(v)} = 33.6 \text{ J/gmol } ^\circ\text{C}$$

$$C_{p,O_2} = 29.3 \text{ J/gmol } ^\circ\text{C}$$

$$C_{p,N_2} = 29.1 \text{ J/gmol } ^\circ\text{C}$$

where we are using the approximate heat capacities because the net temperature change is not that large. The energy balance equation on the boiler (excluding the tubes) is

$$\dot{Q} = -33.99 \times 10^6 \text{ kJ/h} = \dot{H}_{out} - \dot{H}_{in} = \dot{M}_{M,in} \Delta \hat{H}_{c,M} + \int_{25^\circ\text{C}}^{150^\circ\text{C}} \sum_i n_{i,out} C_{p,i} dT$$

$$-33.99 \times 10^6 \text{ kJ/h} = \dot{M}_{M,in} (-802.6) + \dot{M}_{M,in} [0.037 + 2(0.0336) + 0.4(0.0293) + 9.024(0.0291)](150 - 25)$$

where heat capacities have been converted to kJ/gmol $^\circ\text{C}$, all flows out have been written in terms of methane flow in, and it is assumed that all the methane fed is completely combusted. We solve this equation to find

$$\dot{M}_{M,in} = 45000 \text{ gmol/h} = 45.0 \text{ kgmol/h}$$

The air flow in and the flue gas composition and flow rate can be easily calculated:

Air flow in: 514 kgmol/h

Flue gas: 559 kgmol/h, 8.1% CO_2 , 16.1% H_2O , 3.2% O_2 , 72.6% N_2 (mol%)

P6.83

Condenser: $\dot{Q} = \dot{H}_{out} - \dot{H}_{in}$, \dot{Q} is negative

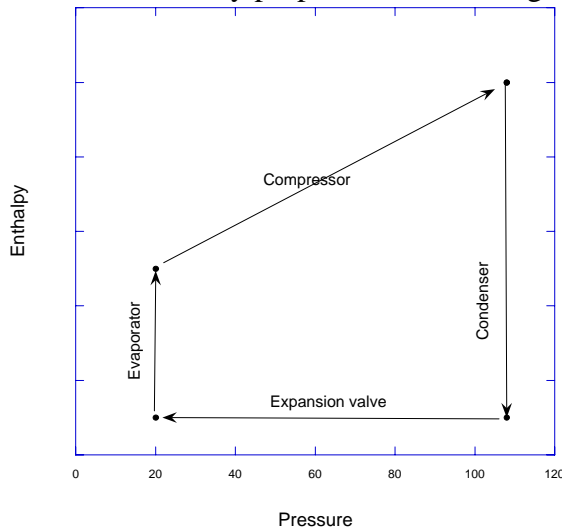
Receiver; $\dot{H}_{out} = \dot{H}_{in}$

Expansion valve: $\dot{H}_{out} = \dot{H}_{in}$

Evaporator: $\dot{Q} = \dot{H}_{out} - \dot{H}_{in}$, \dot{Q} is positive

Compressor: $\dot{W}_s = \dot{H}_{out} - \dot{H}_{in}$, \dot{W}_s is positive

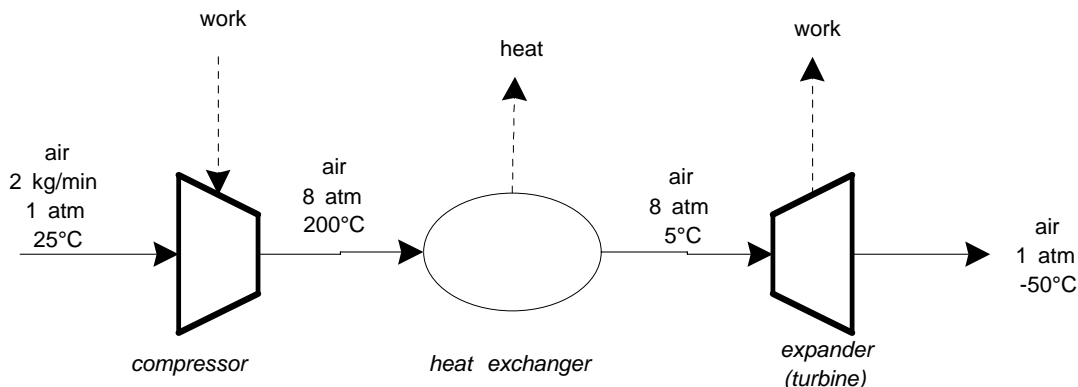
We don't have any properties of the refrigerant but qualitatively the P - H diagram is:



P6.84

(Note to instructor: you may want to direct students to Perry's or another source of information about refrigeration loops.)

The flow diagram for the open-loop air chiller is



I could use an average heat capacity of $\sim 29.2 \text{ J/gmol } ^\circ\text{C}$ for air and treat air as an ideal gas, in which there would be no enthalpy change due to the pressure change. For more accuracy I will look up data in Perry's Chemical Engineers' Handbook on the thermophysical properties of air. By interpolation we find

$$\hat{H} = 296 \text{ kJ/kg at } 298\text{K, } 1 \text{ atm}$$

$$\hat{H} = 475 \text{ kJ/kg at } 473\text{K, } 8 \text{ atm}$$

$$\hat{H} = 276 \text{ kJ/kg at } 278\text{K, } 8 \text{ atm}$$

$$\hat{H} = 223 \text{ kJ/kg at } 223\text{K, } 1 \text{ atm}$$

An energy balance around the compressor yields:

$$\dot{W}_s = \dot{m}(\hat{H}_{out} - \hat{H}_{in}) = 2(475 - 296) = 358 \text{ kJ/min} = 5967 \text{ W}$$

An energy balance around the heat exchanger yields:

$$\dot{Q} = \dot{m}(\hat{H}_{out} - \hat{H}_{in}) = 2(276 - 475) = -398 \text{ kJ/min} = -6633 \text{ W}$$

An energy balance around the turbine yields:

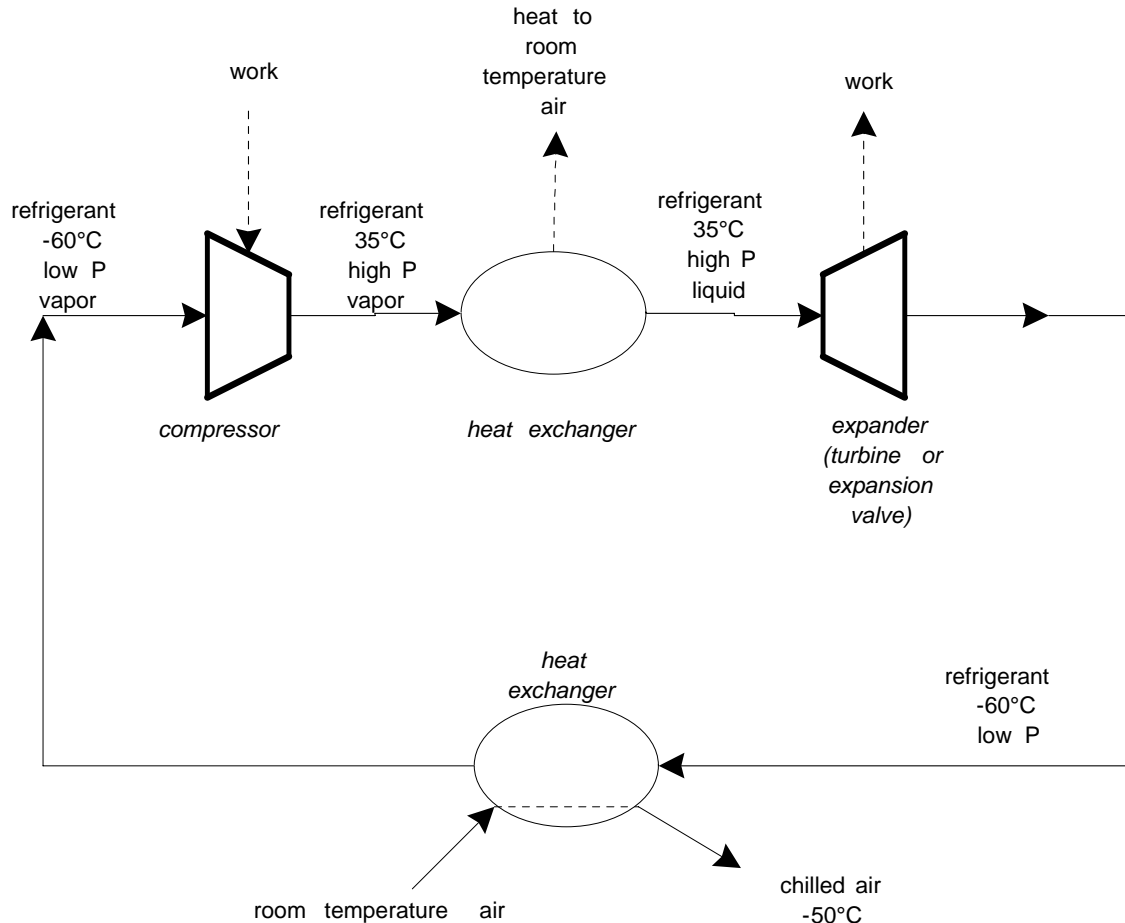
$$\dot{W}_s = \dot{m}(\hat{H}_{out} - \hat{H}_{in}) = 2(223 - 276) = -106 \text{ kJ/min} = -1767 \text{ W}$$

The overall enthalpy change of the air as it goes through this system is:

$$\dot{m}(\hat{H}_{out} - \hat{H}_{in}) = 2(223 - 296) = -146 \text{ kJ/min} = -2433 \text{ W}$$

The net work input to the system is $5967 - 1767 = 4200 \text{ W}$, and we've had to provide cooling at -6633 W , to produce 2 kg/min chilled air at -50°C .

In a typical refrigeration cycle, a refrigerant is circulated through a system similar to that shown in P6.83. To produce chilled air, the operation might look something like this:



We need to know the properties of the refrigerant before we can calculate the net work input of this cycle. But if we look up some information in Perry's Handbook we find that the *best* a refrigeration cycle can do is called the Coefficient of Performance and is calculated as:

$$COP = \frac{T_{cold}}{T_{hot} - T_{cold}} = \frac{Q}{W_{net}}$$

For our system, the cold temperature (chilled air) is $-50^{\circ}\text{C} = 223\text{ K}$ and the hot temperature (room air) is 298 K . Therefore:

$$COP = \frac{T_{cold}}{T_{hot} - T_{cold}} = \frac{223}{298 - 223} = 2.97$$

From this, we estimate that, to provide 2433 W of cooling (the net cooling required for 2 kg/min chilled air), we would require a net work input of $2433/2.97$ or 819 W. This is much less the work input required in the open-loop air chiller.

(a) With the pump as the system, the energy balance is $\dot{W}_s = \dot{m}(\hat{H}_{out} - \hat{H}_{in})$, where “out” and “in” are evaluated from steam tables for water at 10 bar and 1 bar, respectively, and at 50°C: $\dot{W}_s = (10 \text{ kg/s})(210.19 - 209.46 \text{ kJ/kg}) = 7.3 \text{ kJ/s}$.

If the boiler plus the turbine is the system, the energy balance is

$\dot{W}_s + \dot{Q} = \dot{m}(\hat{H}_{out} - \hat{H}_{in})$. The steam leaving the turbine is saturated steam at 1 bar pressure, and the steam entering the system is water at 10 bar and 50°C. Therefore: $\dot{W}_s = \dot{m}(\hat{H}_{out} - \hat{H}_{in}) - \dot{Q} = (10 \text{ kg/s})(2674.9 - 210.19) - 30,000 = -5353 \text{ kJ/s}$. Therefore the net work difference is $5353 - 7.3$ or 5346 kJ/s and

$$\eta = \frac{5353 - 7.3}{30000} = 0.18$$

(b) Combustion of 1 gmol methane requires 2 gmol oxygen, and produces 1 gmol CO_2 and 2 gmol H_2O . Therefore, with 20% excess oxygen, for every 1 gmol methane fed, 2.4 gmol O_2 and 9.03 gmol N_2 are fed, and the flue gases contain 1 gmol CO_2 , 2 gmol H_2O , 0.4 gmol O_2 and 9.03 gmol N_2 . The mol fraction water in the flue gas $y_w =$

$2/(2+1+0.4+9.03) = 0.16$. If the gas is saturated with water vapor (that is, at its dewpoint),

$p_w = y_w P = 0.16(760 \text{ mmHg}) = 122 \text{ mmHg} = P_w^{sat}$. From the Antoine equation:

$\log P_w^{sat} = 8.10765 - \frac{1750.286}{T + 235} = 2.09$, or $T = 55.7^\circ\text{C}$. The flue gases must be cooled to no

lower than 55.7°C to avoid water condensation.

From App. B, the enthalpy of combustion of methane with condensed water is:

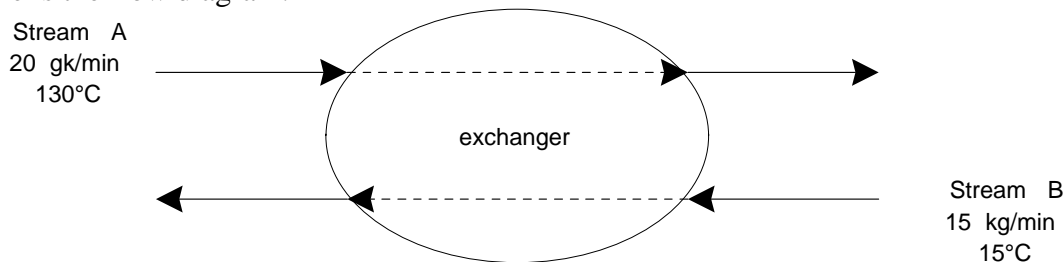
$\Delta\hat{H}_c^\circ = -802.6 + 2(-44) = -890.6 \text{ kJ/gmol}$. This is the maximum enthalpy transferred, if the flue gases are cooled to 25°C and all water is condensed. If water is not condensed, and the gases are cooled to only 55.7°C , we calculate that

$\Delta\hat{H}_c^\circ = -802.6 + \sum m_i C_{p,i} (55.7 - 25) = -791 \text{ kJ/gmol}$ (using approximate C_p values from

App. B). Therefore $\eta_T = \frac{791}{890.6} = 0.89$.

P6.86

Here is the flow diagram:



The energy balance equation considering just stream A as the system is:

$$20(2.4)(T_{out,A} - 130) = -\dot{Q}$$

and the energy balance equation considering just stream B is:

$$15(4.5)(T_{out,B} - 15) = \dot{Q}$$

where we've defined the heat term so that it is the same in both equations, since the heat removed from stream A is exactly equal to and opposite in sign from the heat added to stream B.

The design equation for the heat exchanger is

$$\dot{Q} = UA\Delta T_{lm} = 400(4) \left[\frac{(130 - T_{out,B}) - (T_{out,A} - 15)}{\ln \left(\frac{(130 - T_{out,B})}{(T_{out,A} - 15)} \right)} \right]$$

All 3 equations must be satisfied simultaneously. We use an equation solver to find:

$$\dot{Q} = 5520 \text{ kJ/min}$$

$$T_{out,A} = 15.002^\circ\text{C}$$

$$T_{out,B} = 96.78^\circ\text{C}$$

The exchanger is large enough for the two streams on the right hand side to reach nearly the same temperature. This is an unusually large exchanger! More typically, such a large exchanger cannot be economically justified. If the area drops to 0.4 m^2 , the outlet temperatures change to 32.4 and 84.4°C for streams A and B, respectively, and the heat transferred decreases slightly, to about 4680 kJ/min . But, a factor of 10 reduction in area will greatly reduce the cost of the heat exchanger!

P6.87

(a) The heat to be removed from the hot oil is

$$\dot{Q} = (10000 \text{ lb/h})(0.8 \text{ Btu/lb}^\circ\text{F})(100 - 200^\circ\text{F}) = -800,000 \text{ Btu/h}$$

This is equivalent to the heat to be added to the cooling water. The outlet temperature of the cooling water is calculated from:

$$\dot{Q} = (6000 \text{ lb/h})(1.0 \text{ Btu/lb}^\circ\text{F})(T_{out} - 60^\circ\text{F}) = +800,000 \text{ Btu/h}$$

$$T_{out} = 193^\circ\text{F}$$

The area of heat exchange required is calculated from:

$$\dot{Q} = 800,000 = UA\Delta T_{lm} = 100A \left[\frac{(200 - 193) - (100 - 60)}{\ln \left(\frac{(200 - 193)}{(100 - 60)} \right)} \right]$$

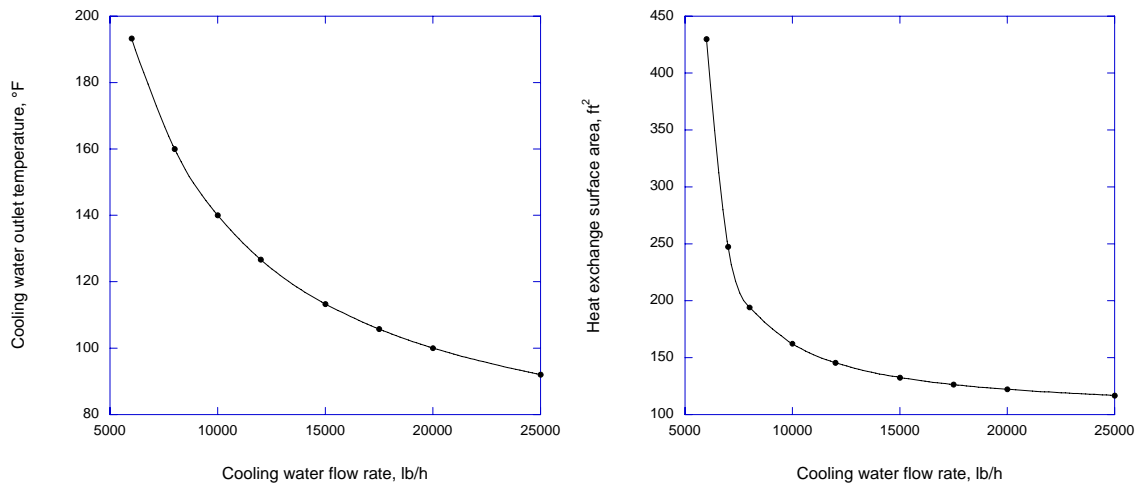
$$A = 430 \text{ ft}^2$$

(b) Since we can vary the cooling water flow rate, we've got two equations in two unknowns:

$$\dot{Q} = (\dot{m}_{cw})(1.0 \text{ Btu/lb}^\circ\text{F})(T_{out} - 60^\circ\text{F}) = +800,000 \text{ Btu/h}$$

$$\dot{Q} = 800,000 = 100A \left[\frac{(200 - T_{out}) - (100 - 60)}{\ln \left(\frac{(200 - T_{out})}{(100 - 60)} \right)} \right]$$

These calculations were set up on a spread sheet, and the flow rate of cooling water was varied. The results are plotted:



As the cooling water flow increases, the outlet temperature of the water decreases. The effect of this is to increase the temperature difference between the hot oil entering the exchanger and the cooling water leaving the exchanger. The increase in temperature difference reduces the area required. The heat exchanger size drops dramatically with a slight increase in the cooling water flow rate from 6000 to 7000 lb/h. The decrease in size is less dramatic with even larger increases. An increase in flow to 7000 or 8000 lb/h would likely be justified by the reduction in the area (and hence the cost) of the heat exchanger.

P6.88

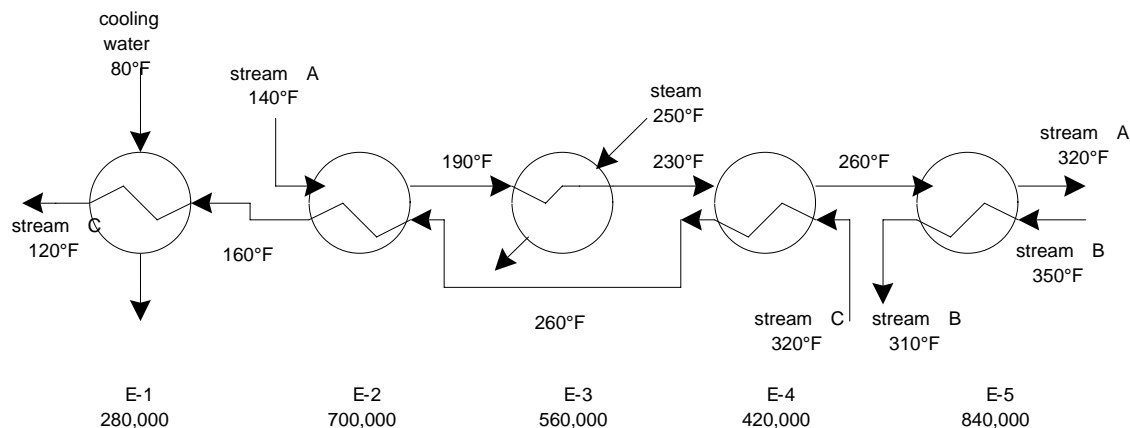
One serious problem with this proposed design is that there is a temperature cross – supposedly, stream A is heated from 140°F to 240°F by cooling stream C from 320°F to 120°F. But, heat doesn't travel from cold to hot! This network as sketched is impossible.

Cooling of stream B should not be achieved by heat exchange with cooling water. Stream B is warm, and we can use some of that heat removal to heat up stream A. This should reduce the steam requirements. We will use cooling water only to do the final cooling of Stream C. We don't need to use 550°F steam to heat, since the hottest temperature we need to reach is only 320°F. We can use 350°F steam (if required).

Next, we calculate the required heat input or output for each stream from $mC_p\Delta T$: for stream A, +2,520,000 Btu/h; for stream B, -840,000 Btu/h; for stream C, -1,400,000 Btu/h. The total heat required to be added to the network is 280,000 Btu/h more than the total to be removed, so we will need to use a bit of steam. Since both stream B and C are pretty warm, perhaps we can use only the cheapest 250°F steam. We will need to use some cooling water, because stream C needs to be cooled to 120°F, and stream A enters the network at a 140°F.

To complete our design, we will assume a 20°F approach temperature (minimum temperature difference between 2 streams exchanging heat). We will first provide as much heat exchange as possible between the streams, using steam and cooling water only as a last resort.

After some iteration, we come up with the following network that satisfies all energy balances and design requirements, and uses cheap steam.



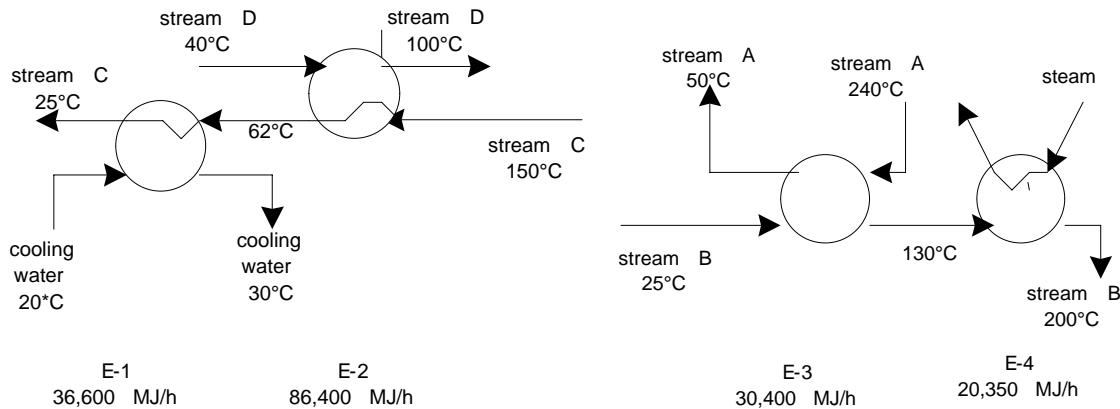
The Btu/h exchanged in each heat exchanger is listed. The network requires 280,000 Btu/h cooling provided by cooling water, and 560,000 Btu/h heating provided by 250°F steam. As originally designed, the network required 840,000 Btu/h cooling, and 1,075,200 Btu/h heating provided by expensive 550°F. The new network requires 5 exchangers instead of 3, but the energy savings are very large.

P6.89

First, we note that there are 2 streams to be cooled (A and C) and 2 streams to be heated (B and D). Stream B does not have to be heated as hot as stream A inlet, so it is reasonable to use stream A to provide at least some of the heating for stream B. Note also that streams A and B are relatively small energy flows (flow rate times heat capacity) while C and D are larger. It might make sense to pair A with B and C with D.

We calculate the required heat input or output for each stream from $mC_p\Delta T$: for stream A, -30,400 MJ/h; for stream B, +50,750 kJ/h; for stream C, -123,000 MJ/h and for stream D, +86,400 MJ/h. Overall we need to remove heat from the network, so some cooling water will definitely be required. If steam is needed, it is available at 250°C (40 bar saturated steam).

Once we start investigating alternatives, it becomes apparent that avoiding a temperature cross in the (A-B) heat exchanger is a problem. It looks like we can't avoid using some steam. We come up with the following solution:



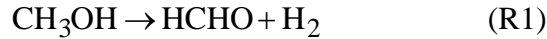
We assumed a 10°C increase in temperature of the cooling water in E-1. The cooling water flow rate required is therefore ~915,000 kg/h, assuming a heat capacity of 4 kJ/kg °C. Assuming steam condenses to saturated liquid in E-4, the steam requirement is 12,000 kg/h. There are other possible configurations that require less steam and cooling water, but these may require more heat exchangers, or larger exchangers.

Given a heat transfer coefficient of 300 kJ/m² h °C for each exchangers, and the temperatures shown on the diagram, we calculate the area of each exchanger from Eq. 6.24.

Exchanger	Q (MJ/h)	ΔT_{lm} (°C)	A (m ²)
E-1	36,600	14.55	7900
E-2	86,400	34.1	8445
E-3	30,400	57.4	1765
E-4	20,350	80.0	850

P6.90

(a) For the proposed modification, the two reactions are



Material balance equations are:

$$\dot{m}_{M,out} = 1000 - \dot{\xi}_1 = 0 \quad \rightarrow \dot{\xi}_1 = 1000$$

$$\dot{m}_{F,out} = \dot{\xi}_1 = 1000$$

$$\dot{m}_{H,out} = \dot{\xi}_1 - \dot{\xi}_2 = 1000 - \dot{\xi}_2$$

$$\dot{m}_{W,out} = \dot{\xi}_2$$

and

$$\dot{m}_{O,in} = \frac{1}{2} \dot{\xi}_2$$

$$\dot{m}_{N,out} = \dot{m}_{N,in} = 3.76 \dot{m}_{O,in}$$

The reactor is proposed to operate adiabatically, therefore the energy balance simplifies to

$$\dot{H}_{out} - \dot{H}_{in} = 0$$

We construct a pathway to calculate the change in enthalpy: we cool the reactants from T_{in} (250°C) to 25°C (in vapor phase), then react by R1 and R2 at 25°C, then heat the products up from 25°C to T_{out} (150°C). In equation form:

$$\begin{aligned} \dot{H}_{out} - \dot{H}_{in} = 0 = & \left[\dot{m}_{M,in} C_{p,M} + \dot{m}_{N,in} C_{p,N} + \dot{m}_{O,in} C_{p,O} \right] (25 - T_{in}) + \dot{\xi}_1 \Delta \hat{H}_{r1}^\circ + \dot{\xi}_2 \Delta \hat{H}_{r2}^\circ \\ & + \left[\dot{m}_{F,out} C_{p,F} + \dot{m}_{N,out} C_{p,N} + \dot{m}_{H,out} C_{p,H} + \dot{m}_{W,out} C_{p,W} \right] (T_{out} - 25) \end{aligned}$$

where we use the approximate heat capacities (and therefore get an approximate answer).

We look up physical property data in the Appendix;

$$\Delta \hat{H}_{r1}^\circ = 200.94 - 108.6 = 92.3 \text{ kJ/gmol}$$

$$\Delta \hat{H}_{r2}^\circ = -241.83 \text{ kJ/gmol}$$

$$\begin{aligned}
C_{p,M} &= 43.9 \text{ J/gmol } ^\circ\text{C} \\
C_{p,O} &= 29.3 \text{ J/gmol } ^\circ\text{C} \\
C_{p,N} &= 29.1 \text{ J/gmol } ^\circ\text{C} \\
C_{p,F} &= 35.4 \text{ J/gmol } ^\circ\text{C} \\
C_{p,H} &= 29.1 \text{ J/gmol } ^\circ\text{C} \\
C_{p,W} &= 33.6 \text{ J/gmol } ^\circ\text{C}
\end{aligned}
\quad (\text{all in the vapor phase})$$

Now we substitute in the data as well as the material balance equations and find:

$$\begin{aligned}
0 = & \left[1000(43.9) + \frac{3.76}{2} \dot{\xi}_2(29.1) + \frac{1}{2} \dot{\xi}_2(29.3) \right] (25 - 250) + (1000)(92,300) + \dot{\xi}_2(-241,830) \\
& + \left[(1000)(35.4) + \frac{3.76}{2} \dot{\xi}_2(29.1) + (1000 - \dot{\xi}_2)(29.1) + \dot{\xi}_2(33.6) \right] (150 - 25)
\end{aligned}$$

We solve to find:

$$\dot{\xi}_2 = 413.5 \text{ gmol/min}$$

(b) The obvious safety hazard is that we are mixing oxygen with a hot organic stream. Fires and explosions are possible. There is also the concern that the reaction will not be controlled and complete oxidation of methanol to CO_2 and H_2O could occur. Besides the obvious concern that no product would be made, there is the other concern that methanol oxidation is very exothermic, and we could be faced with a runaway reaction, where the reactor temperature could get very high. If the air was carefully metered into the reactor, so that the oxygen content was kept very low, the likelihood of a runaway reaction is lessened. Also, selection of a catalyst that favors methanol dehydrogenation and not oxidation would greatly help, if such a catalyst were available. Finally, recycling the nitrogen through the reactor, or providing another inert gas, would help to reduce the likelihood of an unsafe increase in reactor temperature.

The net environmental impact depends in large part on how the steam is produced. If fossil fuels were used (as is most common), then CO_2 would be produced in generating the steam. By using (R2) we are essentially replacing combustion of fossil fuels (in the boiler where the steam was produced) by combustion of hydrogen.

(c) The flow of nitrogen through the reactor is significant. The reactor volume required for the proposed process would therefore need to be increased to maintain the same throughput. Another problem is that we have additional separation problems. It should be relatively easy to separate formaldehyde from water, since their boiling points are quite different, but separating formaldehyde from nitrogen may be expensive, depending on what technologies are available. Another consideration is: what was the hydrogen in the existing process used for? If the hydrogen is needed somewhere else in the facility, then there would have to be another source found to replace that used up in (R2). The idea is attractive but more information is needed.