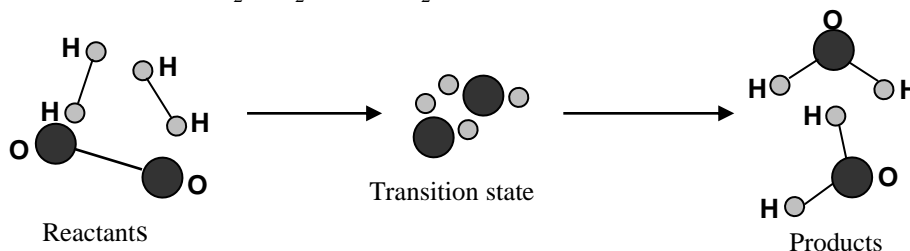


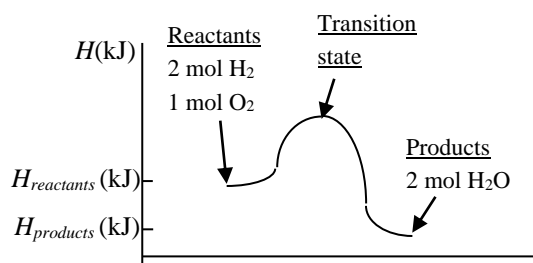
## Section 7: FR&B, Ch. 9 (Energy Balances - III)

### Heat of reaction (Section 9.1)

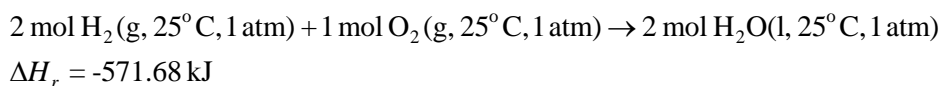
Consider the reaction:  $2\text{H}_2 + \text{O}_2 \longrightarrow 2\text{H}_2\text{O}$



- One O-O bond and two H-H bonds broken. System absorbs energy,  $U_{\text{system}}$  and  $H_{\text{system}}$  increase from reactants to transition state
- 4 O-H bonds are formed. System releases energy,  $U_{\text{system}}$  and  $H_{\text{system}}$  decrease from transition state to products.
- Suppose stoichiometric quantities of the reactants (2 mol  $\text{H}_2$  + 1 mol  $\text{O}_2$ ) react completely, with the reactants starting at  $T$  and  $P$  and the products (2 mol  $\text{H}_2\text{O}$ ) ending at the same  $T$  and  $P$ . Plot the enthalpy of the reaction system at the three stages of the process.

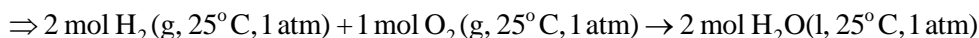


- The change in enthalpy from reactants to products,  $H_{\text{products}} - H_{\text{reactants}} = \Delta H_r(T, P)$ , is the *heat of reaction*. For stoichiometric quantities of  $\text{H}_2$  and  $\text{O}_2$  reacting completely at  $T=25^\circ\text{C}$  and  $P=1$  atm,



- Negative  $\Delta H_r \Rightarrow (\text{Energy})_{\text{products}} < (\text{Energy})_{\text{reactants}} \Rightarrow$  more energy released by product bond formation than absorbed when reactant bonds break. The reaction is therefore *exothermic*.

Shorthand notation :  $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l}), \Delta H_r^\circ = -571.68 \text{ kJ}$



$$\Delta H_r^\circ = \frac{-571.68 \text{ kJ}}{2 \text{ mol H}_2 \text{ react}} = \frac{-571.68 \text{ kJ}}{1 \text{ mol O}_2 \text{ react}} = \frac{-571.68 \text{ kJ}}{2 \text{ mol H}_2\text{O formed}}$$

- If 5 mol  $\text{H}_2/\text{s}$  react and the reactants and products are at  $25^\circ\text{C}$ , then the energy balance is

$$\dot{Q} = \Delta \dot{H} = \left( \frac{5 \text{ mol H}_2 \text{ react}}{\text{s}} \right) \left( \frac{-571.68 \text{ kJ}}{2 \text{ mol H}_2 \text{ react}} \right) = -1430 \frac{\text{kJ}}{\text{s}} = -1430 \text{ kW} \quad (\text{The reactor must be cooled})$$

## Section 7: F&R, Ch. 9 (Energy Balances – III)

- $\Delta H_r^\circ$  (kJ) is the *standard heat of reaction*, the heat of the reaction with the given stoichiometry, reacting completely, at a reference temperature and pressure of 25°C and 1 atm. (The “standard” part, which refers to the specified temperature and pressure, is denoted by the superscript °.)
- If A is a reactant or product,  $\nu_A$  is its stoichiometric coefficient (negative for reactant, positive for product), and  $n_{A,r}$  (mol A) is a quantity of species A that is either generated or consumed at 25°C, then the enthalpy change is

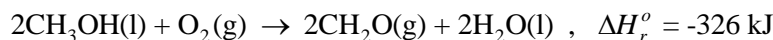
$$\Delta H(kJ) = \frac{\Delta H_r(T_0, P_0)(kJ)}{\nu_i(\text{mol } i)} (n_i - n_{i0})(\text{mol } i) = \frac{n_{ir}}{|\nu_i|} \Delta H_r(T_0, P_0)$$

$$\Delta H(kJ) = \xi \Delta H_r$$

where  $\xi$  is the extent of reaction, defined on p. 496, and  $n_{ir}$  is the amount of species *I* that has been either been consumed or produced by the reaction. For an open system, dots would go above the *H*, *n*, and  $\nu$ . Verify that the water formation reaction example we just did fits this equation.

- Note the properties of the heat of reaction listed in Section 9.1 (exothermic reaction if negative, endothermic if positive; nearly independent of pressure; the standard heat of the reaction  $2A \rightarrow 2B$  is twice that of  $A \rightarrow B$ ).

### Example: Formation of formaldehyde from methanol



(a) This reaction is \_\_\_ exothermic    \_\_\_ endothermic

When it occurs with  $\text{CH}_3\text{OH}$  and  $\text{O}_2$  fed at 25°C, the reactor must be \_\_\_ heated    \_\_\_ cooled to bring the product temperature back to 25°C. If there is no external heating or cooling, then the temperature of the reactor contents will \_\_\_ increase    \_\_\_ decrease.

(b) How many moles of  $\text{O}_2$  would you need if you had 200 moles of  $\text{CH}_3\text{OH}$  react? \_\_\_\_\_

If the heat of reaction is -326 kJ, how would we calculate the enthalpy change?

$\Delta H_r^\circ = -326 \text{ kJ}$  can be interpreted as -326 kJ being generated when *exactly* 2 moles of  $\text{CH}_3\text{OH}$  react with exactly 1 mole of  $\text{O}_2$ . If 4 moles react with 2 moles, the number doubles. If 200 moles react with 100 moles, then the number goes up by a factor of 100...and so on.

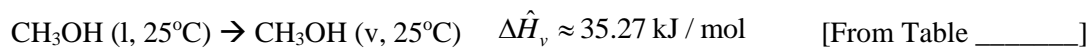
(c)  $4\text{CH}_3\text{OH}(l) + 2\text{O}_2(g) \rightarrow 4\text{CH}_2\text{O}(g) + 4\text{H}_2\text{O}(l) \quad , \quad \Delta H_r^\circ = \underline{\hspace{2cm}} \text{ kJ}$

(d)  $2\text{CH}_3\text{OH}(v) + \text{O}_2(g) \rightarrow 2\text{CH}_2\text{O}(g) + 2\text{H}_2\text{O}(v) \quad , \quad \Delta H_r^\circ = \underline{\hspace{2cm}} \text{ kJ}$

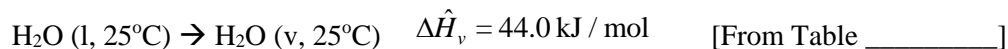
## Section 7: F&amp;R, Ch. 9 (Energy Balances – III)

To do this calculation, we need to know the heats of vaporization of methanol and water at 25°C.

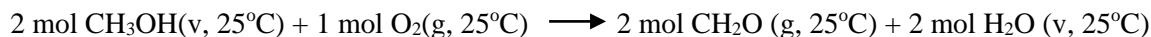
Estimate them from data in the text.



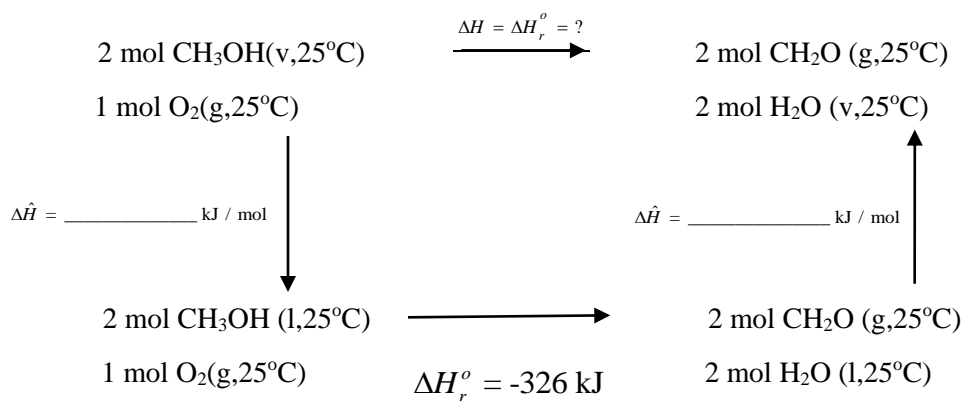
[Assumed \_\_\_\_\_]



The quantity we seek is the enthalpy change for the process



To find it, construct a process path that makes use of known enthalpy changes.



The desired heat of reaction is then

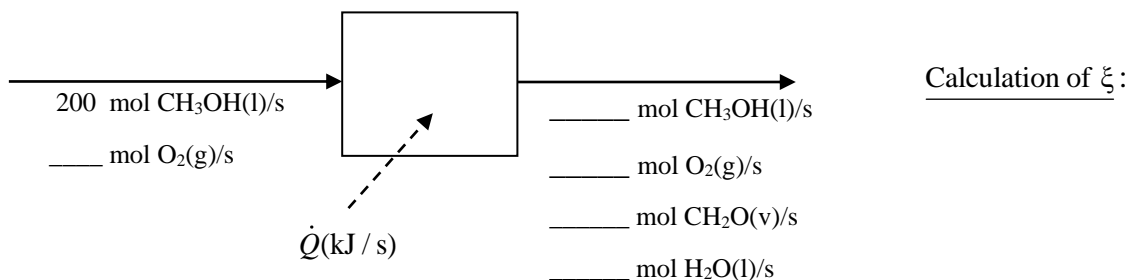
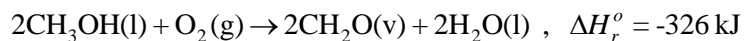
$$\Delta H_r^o = \sum \Delta H =$$

$$= -309 \text{ kJ}$$

**(d)** How could we calculate a more accurate value of  $\Delta\hat{H}_v$  of methanol at 25°C from data in the text?

## Section 7: F&R, Ch. 9 (Energy Balances – III)

- (e) Suppose 200 mol/s of liquid methanol and 30% excess oxygen are fed to a reactor at 25°C, a 50% fractional conversion of methanol is obtained, and the products are brought back down to 25°C. You wish to calculate  $\dot{Q}(\text{kJ} / \text{s})$ . Here is the flow chart.

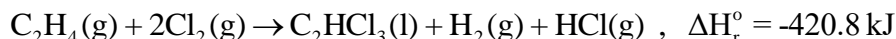


Do a DOF and solve unknowns. Then calculate  $\xi$ . Finally, in the space below, write and simplify the energy balance equation and calculate the required rate of heat transfer.

## Section 7: F&R, Ch. 9 (Energy Balances – III)

### Internal energy of reaction

Suppose the reaction in which ethylene is chlorinated to form trichloroethylene



takes place in a batch (closed) reactor at constant volume. The closed system energy balance involves internal energies, not enthalpies, and so we'll need to evaluate  $\Delta U_r$ , the internal energy change when 1 mol of ethylene and 2 mol of chlorine react completely. What we are likely to know, however, is the enthalpy change for that process (the heat of reaction). The question is, how can we get the first one from the known value of the second one?

- For any system,  $H = U + PV$ , and for any change in the system state (including reaction),

$$\Delta H = \Delta U + \Delta(PV)$$

or solving for  $\Delta U$  and applying the result to our reaction process

$$\Delta U_r = \Delta H_r - \Delta PV$$

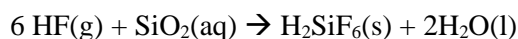
- In general, for any reaction in which stoichiometric quantities of reactants react completely (which is what is involved when dealing with standard heats of reaction) and the stoichiometric coefficient of Species  $i$  is  $\nu_i$ ,

$$\Delta PV \approx (PV)_{\text{gaseous products}} - (PV)_{\text{gaseous reactants}} = RT \sum_{\text{gaseous products}} |\nu_i| - RT \sum_{\text{gaseous reactants}} |\nu_i|$$

$$\text{and} \quad \Delta U_r \approx \Delta H_r - RT \left( \sum_{\text{gaseous products}} |\nu_i| - \sum_{\text{gaseous reactants}} |\nu_i| \right) \quad (9.1-5) \quad \text{(Verify that this formula works for the example reaction.)}$$

If a reaction has no gaseous products or reactants, to a good approximation  $\Delta U_r = \Delta H_r$ .

Exercise: Write an expression for  $\Delta \hat{U}_r$  in terms of  $\Delta \hat{H}_r$  and  $T$  for the reaction in which gaseous hydrogen fluoride reacts with dissolved silica:

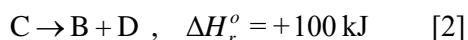
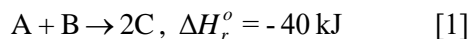


$$\Delta U_r = \underline{\hspace{2cm}}$$

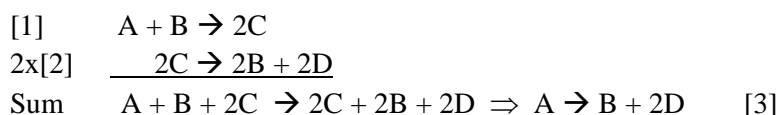
## Section 7: F&R, Ch. 9 (Energy Balances – III)

### Hess's Law (Section 9.2)

Hess's law states that if you can obtain a stoichiometric equation as a linear combination of the stoichiometric equations for other reactions, you can determine its heat of reaction by performing the same operations on the heats of the other reactions. For example, suppose we experimentally determine the following two standard heats of reaction:



We want to determine the heat of the reaction  $A \rightarrow B + 2D$  but can't carry out that reaction experimentally. We observe, however, that we can obtain that stoichiometric reaction as  $[1] + 2x[2]$ :



Therefore

$$(\Delta H_r^\circ)_3 = (\Delta H_r^\circ)_1 + 2(\Delta H_r^\circ)_2 = -40 \text{ kJ} + 2(100 \text{ kJ}) = 160 \text{ kJ}$$

Hess's law follows from the fact that enthalpy is a state function. An illustration of how and why it works is given in Section 9.2 of the text.

- *Why do we care?* Because some reactions cannot be carried out in isolation (that is, without side reactions occurring simultaneously) so that their heat of reaction can't be measured directly, but other reactions for which the heat of reaction *can* be measured can be combined linearly to get the reaction we want. The CO formation reaction described in Section 9.2 provides an illustration.
- Work through Example 9.2-1 and the Test Yourself that follows it.

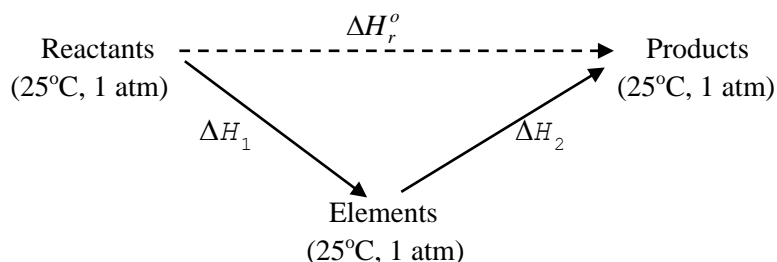
## Calculating Heats of Reaction from Heats of Formation (Section 9.3)

- Formation reaction:** A reaction in which a compound is formed from its elemental constituents as they occur in nature [e.g.,  $\text{O}_2(\text{g})$ , and not  $\text{O}$ ]. The *standard heat of formation*,  $\Delta\hat{H}_f^\circ$ , is the standard heat of such a reaction. Standard heats of formation of many species are given in Table B.1 or using APEX functions DeltaHfg, DeltaHfl, DeltaHfc, or DeltaHfaq.

$$\begin{aligned} (\Delta\hat{H}_f^\circ)_{\text{CH}_5\text{N}(\text{g})} &= -28.0 \frac{\text{kJ}}{\text{mol}} \\ \Rightarrow \text{C}(\text{s}) + \frac{5}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{N}_2 &\rightarrow \text{CH}_5\text{N}(\text{g}), \Delta H_r(25^\circ\text{C}, 1\text{ atm}) = -28.0\text{ kJ} \end{aligned}$$

The standard heat of formation of an elemental species [ $\text{C}(\text{s})$ ,  $\text{H}_2(\text{g})$ ,  $\text{O}_2(\text{g})$ ,...] is zero.

- You can use Hess's law to show that for *any* reaction a hypothetical process path can be drawn from reactants to elements to products::



You should be able to convince yourself that

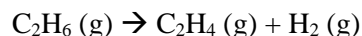
$$\Delta H_1 = - \sum_{\text{reactants}} |\nu_i| \Delta\hat{H}_{fi}^\circ \quad \text{and} \quad \Delta H_2 = \sum_{\text{products}} |\nu_i| \Delta\hat{H}_{fi}^\circ$$

and since enthalpy is a state function,  $\Delta H_r = \Delta H_1 + \Delta H_2$ , from which Eq. (9.3-1) follows.

$$\Delta H_r^\circ = \sum_{\text{products}} |\nu_i| \Delta\hat{H}_{fi}^\circ - \sum_{\text{reactants}} |\nu_i| \Delta\hat{H}_{fi}^\circ \quad (9.3-1)$$

where  $\nu_i$  is the stoichiometric coefficient of the  $i^{\text{th}}$  reactant or product species and  $\Delta\hat{H}_{fi}^\circ$  is the standard heat of formation of that species.

**Exercise:** Use heats of formation to calculate the standard heat of the reaction:



**Solution:**  $\Delta H_r^\circ =$

Work through Example 9.3-1 and the Test Yourself that follows it.

## Calculating Heats of Reaction from Heats of Combustion (Section 9.4)

- *Standard heat of combustion:* Standard heat of the complete combustion of a fuel to form CO<sub>2</sub>(g) and H<sub>2</sub>O(l) (+ S in fuel → SO<sub>2</sub>, N in fuel → N<sub>2</sub>), with reactants and products at 25°C and 1 atm. Standard heats of combustion can be found in Table B-1 or using APEX functions DeltaHcg, DeltaHcl, DeltaHcc, or DeltaHcs.

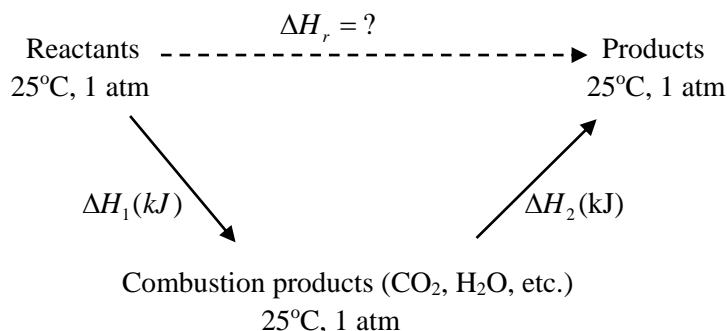
$$\begin{aligned} \left( \Delta \hat{H}_c^o \right)_{\text{C}_3\text{H}_6\text{O}(\text{g})} &\stackrel{\text{Table B.1}}{=} -1821.4 \frac{\text{kJ}}{\text{mol}} \\ \Rightarrow 1 \text{ mol C}_3\text{H}_6\text{O}(\text{g}) + 4 \text{ mol O}_2(\text{g}) &\rightarrow 3 \text{ mol CO}_2(\text{g}) + 3 \text{ mol H}_2\text{O}(\text{l}) \end{aligned}$$

- If a reaction only involves combustible reactants and products, then we can calculate the standard heat of the reaction from tabulated standard heats of combustion. The formula is

$$\Delta H_r^o = \sum_{\text{reactants}} |v_i| \Delta \hat{H}_{ci}^o - \sum_{\text{products}} |v_i| \Delta \hat{H}_{ci}^o \quad (9.4-1)$$

where  $v_i$  is the stoichiometric coefficient of the  $i^{\text{th}}$  reactant or product species and  $\Delta \hat{H}_{ci}^o$  is the standard heat of combustion of that species. The formula looks like the one involving heats of formation, except that the summations are reversed (reactants - products).

This formula is derived from Hess's law in the same way that the heat of formation formula was derived:

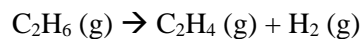


Any reactants or products that are themselves combustion products (CO<sub>2</sub>, H<sub>2</sub>O(l), SO<sub>2</sub>...) have a zero heat of combustion. (See Example 9.4-1 for a derivation of the formula using Hess's law.)



## Section 7: F&R, Ch. 9 (Energy Balances – III)

Exercise: Use heats of combustion to calculate the standard heat of the ethane dehydrogenation reaction:



Solution:  $\Delta H_r^\circ =$

*How are heats of reaction (including heats of formation and heats of combustion) measured?*

Heat of combustion can be measured experimentally in a calorimeter with some known initial temperature and final temperature. Standard heat of combustion can then be determined by calculating the sensible heat required to bring the reactants from standard conditions to the initial condition in the calorimeter, adding the measured heat of combustion, and then adding the sensible heat required to bring the products back down to standard conditions. These standard heats of combustion are tabulated in Table B.1, Perry's Handbook, APEX functions DeltaHcg, DeltaHcl, DeltaHcc, and DeltaHcs.

Some standard heats of formation (like that of water) can sometimes be measured directly in a calorimeter; others can be determined from standard heats of combustion; still others by measuring heats of reaction for which all but one heat of formation is known. Those are also tabulated. The standard heat of any reaction can then be determined from either tabulated heats of formation or heats of combustion.

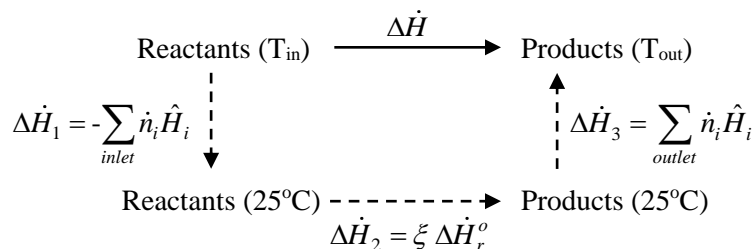
## Section 7: F&R, Ch. 9 (Energy Balances – III)

- Energy balance equation for heat of reaction method**

Closed system:  $Q + W = \Delta U + \Delta E_k + \Delta E_p$  where  $\Delta U = \xi \Delta U_r^o + \sum_{final} n_i \hat{U}_i - \sum_{initial} n_i \hat{U}_i$

Open system:  $\dot{Q} + \dot{W}_s = \Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p$  where  $\Delta \dot{H} = \xi \Delta \dot{H}_r^o + \sum_{out} \dot{n}_i \hat{H}_i - \sum_{in} \dot{n}_i \hat{H}_i$

The process path that leads to this expression for  $\Delta \dot{H}$  (recalling that the reference states are the reactants and products at 25°C and 1 atm) is



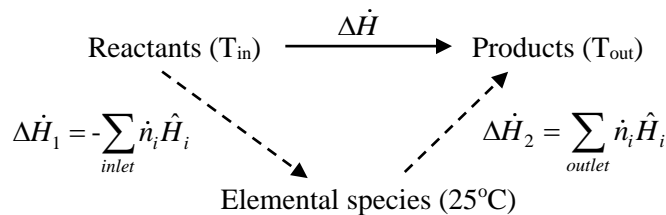
Writing  $\Delta \dot{H} = \Delta \dot{H}_1 + \Delta \dot{H}_2 + \Delta \dot{H}_3$  and substituting for each of the three enthalpy changes on the right leads to the given expression for  $\Delta \dot{H}$ . See illustration in Section 9.5 and Example 9.5 - 1.

- Energy balance equation for heat of formation method:**

Closed system:  $Q + W = \Delta U + \Delta E_k + \Delta E_p$  where  $\Delta U = \sum_{final} n_i \hat{U}_i - \sum_{initial} n_i \hat{U}_i$

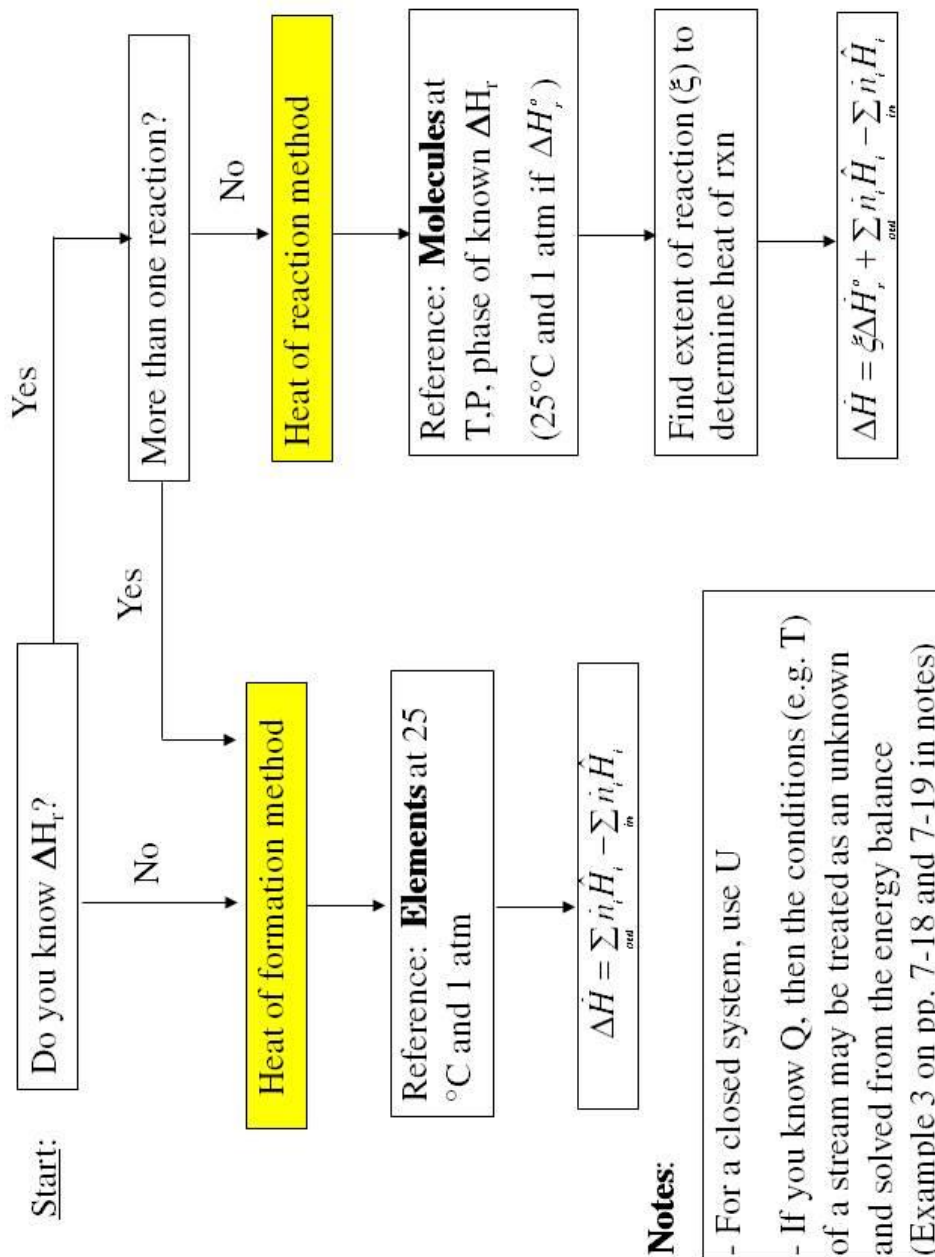
Open system:  $\dot{Q} + \dot{W}_s = \Delta \dot{H} + \Delta \dot{E}_k + \Delta \dot{E}_p$  where  $\Delta \dot{H} = \sum_{out} \dot{n}_i \hat{H}_i - \sum_{in} \dot{n}_i \hat{H}_i$

The process path (recalling that the reference states are the elemental species at 25°C and 1 atm) is



Writing  $\Delta \dot{H} = \Delta \dot{H}_1 + \Delta \dot{H}_2$  and substituting for each of the two enthalpy changes on the right leads to the given expression for  $\Delta \dot{H}$ . See illustration in Section 9.5 and Example 9.5 - 2.

### Calculating $\Delta H$ in a reactive system...Heat of formation or Heat of reaction method?



## Section 7: F&R, Ch. 9 (Energy Balances – III)

### Energy balances on reactive processes (Section 9.5)

Use the following procedure for all energy balance problems in Chapter 9. For a batch (closed) reactor, replace “enthalpy” wherever it occurs with “internal energy.”

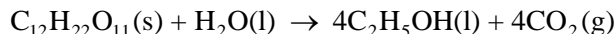
Given a process description:

1. Draw and label the flow chart. Include all known phases, temperatures, pressures in the labeling, as well as heat and (if there is any) work.
2. Do the degree-of-freedom analysis as usual. If a heat, work, or stream temperature is to be determined, include an energy balance among the equations available to solve for the unknowns.
3. Write all the system equations except the energy balance. If the problem is to find  $Q$ , you should be able to solve them for all other unknowns, but if  $Q$  is specified or the system is adiabatic, you will need to add the energy balance to the set of equations to be solved simultaneously.
4. Prepare an inlet-outlet enthalpy table. Choose reference states (phase,  $T$ , and  $P$ ) for each species in the process in the state (phase, temperature, pressure) for which the heat of reaction is known. For reactive species, the references may be the species themselves at 25°C and 1 atm (*heat of reaction method*) or their elemental species in their naturally occurring states at 25°C and 1 atm (*heat of formation method*). *The heat of reaction method is best used for a single reaction with a known standard heat of reaction; for other situations, use the heat of formation method.*
5. In the table, fill in known and labeled amounts or flow rates from the flow chart. If a species is at its reference state, enter zero for the specific enthalpy. If a species does not occur at a given inlet or outlet state, cross out the corresponding cells in the table. Label all remaining specific enthalpies or internal energies ( $\hat{H}_1, \hat{H}_2, \hat{H}_3, \dots$ ).
6. Write the energy balance equation (include the heat of reaction term if molecular species were chosen as references, omit it if elemental species were chosen).
7. Write expressions for all of the labeled specific enthalpies by calculating the enthalpy change for the process in which the species goes from its reference state to the process state. Construct a convenient process state that makes use of the data in the text:
  - Tables B.8 and B.9 for enthalpies of combustion gases.
  - steam tables for enthalpies of liquid water and steam at high pressures (if you use the steam tables, make your reference state for water liquid at the triple point).
  - heat capacities at 1 atm from Table B.2 (use APEx to integrate them), or Kopp’s rule and Table B.10 for a solid or liquid species not listed in Table B.2. If internal energies are being calculated, use Eqs. (8.3-11) and (8.3-12) to convert  $C_p$  to  $C_v$ .
  - heats of fusion and vaporization at the normal boiling point from Table B.1. For species not listed in Table B.1, use one of the estimation formulas on pp. 381–382.
  - heats of mixing and solution at 25°C from Table B.11.
  - heats of formation and combustion at 25°C and 1 atm from Table B.1

Unless huge pressure changes from inlet to outlet are involved, ignore the effect of  $P$  on specific enthalpy and internal energy. Substitute the expressions in the energy balance. Solve all equations.

## Section 7: F&R, Ch. 9 (Energy Balances – III)

**Example 1.** Ethyl alcohol is produced by fermenting maltose (a sugar) in a continuous fermentation process. The reaction is:



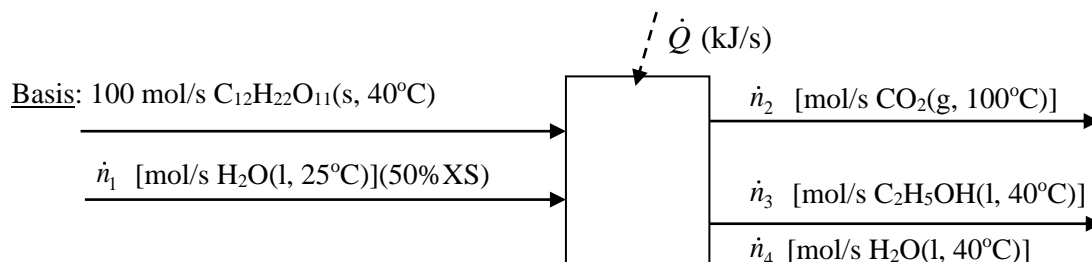
Maltose at 40°C and 50% excess water at 25°C are fed to the process. The maltose reacts completely. The process effluents are liquid ethanol and liquid water at 40°C and carbon dioxide at 100°C. The standard heat of combustion of maltose to form  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{l})$  is  $-5649.1 \text{ kJ/mol}$ . Calculate the standard heat of the reaction, and the required net heat transfer to or from the process (kJ/100 mol maltose fed), using the heat of reaction method for the energy balance.

**Solution:**

Since the heat of formation of maltose is not listed in Table B.1 but we do know the heat of combustion, the only way we have of determining the heat of reaction is by using Equation \_\_\_\_\_.

$\Delta H_r^\circ =$

Following the procedure on p. 7-12, we draw and label the flow chart (Step 1), do the degree of freedom analysis (Step 2), and write all equations but the energy balance (Step 3).



DOF Analysis (base it on extent of rxn balances)

\_\_\_\_\_ unknowns (\_\_\_\_\_)

- \_\_\_\_\_

- \_\_\_\_\_

- \_\_\_\_\_

- \_\_\_\_\_

= 0 DOF

Determine the values of  $n_1$ ,  $n_2$ ,  $n_3$ , and  $n_4$  and write them on the chart, and also calculate  $\xi$ .

$$\dot{n}_1 = \text{_____ mol/s H}_2\text{O}(\text{l}) \text{ , } \dot{n}_2 = \text{_____ mol/s CO}_2(\text{g}) \text{ , } \dot{n}_3 = \text{_____ mol/s C}_2\text{H}_5\text{OH}(\text{l})$$

$$\dot{n}_4 = \text{_____ mol/s H}_2\text{O}(\text{l}) \text{ , } \xi: \text{_____}$$

## Section 7: F&R, Ch. 9 (Energy Balances – III)

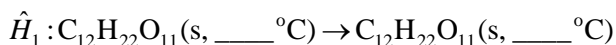
Next, prepare the inlet-outlet enthalpy table, using the Heat of Reaction method. Choose reference states for each species appropriate for the heat of reaction method (Step 4), cross out cells that are not needed, fill in known and labeled  $n$  values from the flow chart, put in zero values for specific enthalpies of any species at their reference states, and label all remaining specific enthalpies (Step 5).

<b>References:</b>				
<b>Species</b>	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ / mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ / mol)
C <sub>12</sub> H <sub>22</sub> O <sub>11</sub>	100	$\hat{H}_1$		
H <sub>2</sub> O				
C <sub>2</sub> H <sub>5</sub> OH				
CO <sub>2</sub>				

Now simplify the energy balance equation and substitute the appropriate expression for  $\Delta H$ .

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

Finally, write formulas for each of the unknown specific enthalpies. (Hints: You will not find maltose in Table B.2, and from the two points given in Table B.2,  $(C_p)_{\text{ethanol(l)}} [\text{kJ}/(\text{mol } ^\circ\text{C})] = 0.1031 + 5.57 \times 10^{-4}T$ .) When the formulas are substituted in the energy balance, all equations can then be solved.



$$C_p \approx \quad \quad \quad = 488.2 \frac{\text{J}}{\text{mol} \times ^\circ\text{C}} = 0.4882 \frac{\text{kJ}}{\text{mol} \times ^\circ\text{C}}$$

$$\hat{H}_1 = \Delta \hat{H} =$$

$$\hat{H}_2 :$$

$$\hat{H}_3 :$$

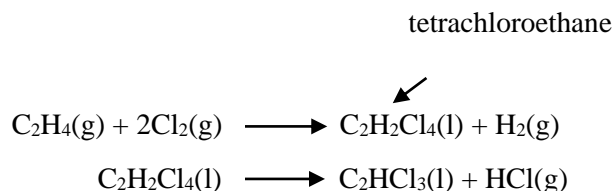
$$\hat{H}_4 :$$

$$\hat{H}_5 :$$

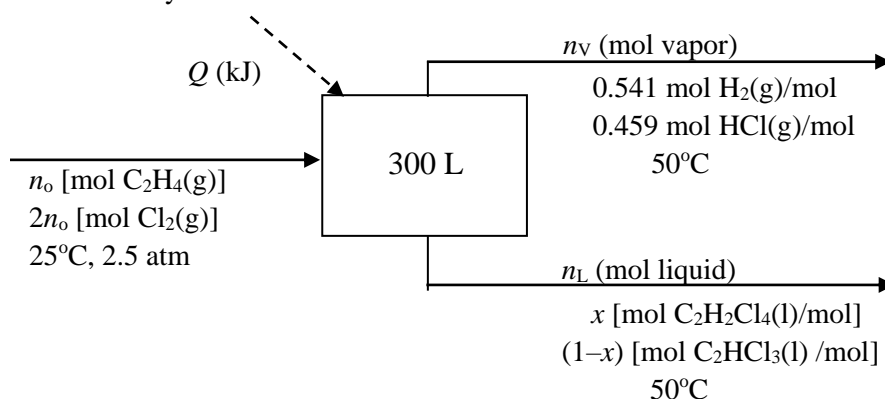
## Section 7: F&R, Ch. 9 (Energy Balances – III)

### Example 2. (Variant of Problem 9.8)

Trichloroethylene, a common degreasing solvent, is produced in the following two-step reaction sequence in a 300-liter batch reactor.



Stoichiometric quantities of ethylene and chlorine are fed to the reactor at 25°C and 2.5 atm. The reactor contents are heated, the reactions proceed, and then the reactor is cooled to a temperature of 50°C and the vapor contents are analyzed. The results are shown below.



Calculate the required heat transfer to or from the reactor, assuming ideal-gas behavior and using the heat of formation method for the energy balance.

### Solution

We have already taken the step of drawing and labeling the flow chart, so we next do the DOF analysis, basing it on atomic balances.

____ unknowns (____)
- ____ - ____ - ____
= 0 DOF

Next, write all system equations but the energy balance, using atomic balances. Identify each equation.

(1)

(2)

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(3)

(4)

We could solve these equations to determine all unknown variables but \_\_\_\_\_, but let's just leave them, write the energy balance, and then solve all of the equations simultaneously. First, prepare the internal energy table (we have a closed system), remembering that we're going to use the heat of formation method. Fill in the references, insert blanks and zeroes where appropriate, fill in molar quantities from the flow chart, and label unknown specific internal energies. Since there are multiple reactions, let's use the heat of formation method.

<b>References:</b>				
<b>Species</b>	$n_{in}$ (mol)	$\hat{U}_{in}$ (kJ / mol)	$n_{out}$ (mol)	$\hat{U}_{out}$ (kJ / mol)
C <sub>2</sub> H <sub>4</sub> (g, 25°C)	$n_o$	$\hat{U}_1$		
Cl <sub>2</sub> (g, 25°C)				
H <sub>2</sub> (g, 50°C)				
HCl (g, 50°C)				
C <sub>2</sub> H <sub>2</sub> Cl <sub>4</sub> (l, 50°C)				
C <sub>2</sub> HCl <sub>3</sub> (l, 50°C)				

Write the energy balance equation, substituting from the table in the expression for  $\Delta U$ .

(5)



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Finally, write expressions for all the labeled specific internal energies in terms of physical property data you can find in the text. (*Assume that you know the standard heats of formation of liquid tetrachloroethane and trichloroethylene, which are not in the text.*) Remember Eqs. (8.3-11) and (8.3-12) for converting  $C_p$  to  $C_v$  and Eq. (9.1-5) for converting heats of reaction to internal energies of reaction.

The first expression is given as an illustration:

$$2\text{C(s, 25}^\circ\text{C)} + 2\text{H}_2\text{(g, 25}^\circ\text{C)} \rightarrow \text{C}_2\text{H}_4\text{(g, 25}^\circ\text{C)}$$

Table B.1  
↙

$$(6) \hat{U}_1 = \Delta \hat{U}_f^o \xrightarrow{\text{Eq. (9.1-5)}} \left( \Delta \hat{H}_f^o \right)_{\text{C}_2\text{H}_4} - RT(1 - 2) = 52.28 \frac{\text{kJ}}{\text{mol}} + \left( 0.008314 \frac{\text{kJ}}{\text{mol} \times \text{K}} \right) (298\text{K})$$

In writing the remainder of the expressions, you don't have to write out the process as was done in this case, just the expressions for  $\hat{U}_3$ ,  $\hat{U}_4$ ,  $\hat{U}_5$ , and  $\hat{U}_6$ .

(7)

(8)

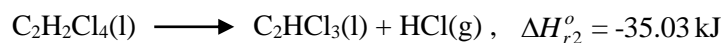
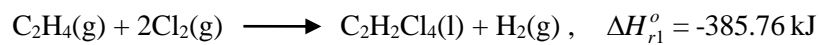
(9)

(10)

Once the heats of formation and heat capacities are substituted into the expressions, APEx can be used to solve Eqs. (1)–(10) simultaneously.

### Section 7: F&R, Ch. 9 (Energy Balances – III)

**Question:** Suppose you are given the standard heats of both reactions:



How would you calculate the standard heats of formation of tetrachloroethane and trichloroethylene to substitute in Eqs. (9) and (10)?

## Section 7: F&R, Ch. 9 (Energy Balances – III)

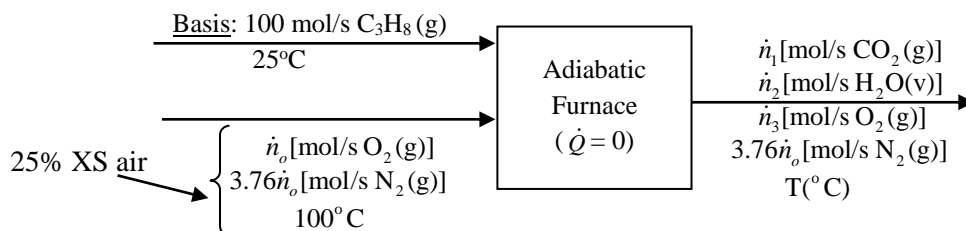
### Example 3—Known Q and Unknown Outlet Conditions (Section 9.5b)

Propane at 25°C is burned with 25% excess air at 100°C in a continuous combustion process. Calculate the maximum stack gas temperature that can be achieved.

**Solution.** Two things happen to the energy released by combustion (i.e., the heat of combustion). Some of it is transferred out of the furnace as heat ( $\dot{Q}$ )—to water inside boiler tubes that pass through the furnace, for example, or through the exterior furnace wall—and the rest goes to heat the combustion product gas and raise its kinetic energy (the latter effect is generally negligible).

- The maximum temperature is achieved when:

- (a) the reactor is \_\_\_\_\_  
and (b) the combustion is \_\_\_\_\_



- DOF Analysis (based on atomic species balances)

<div style="text-align: right; margin-bottom: 10px;">_____ unknowns (_____)</div> <div style="margin-bottom: 10px;">- _____</div> <div style="margin-bottom: 10px;">- _____</div> <div style="margin-bottom: 10px;">- _____</div> <hr style="border: 0.5px solid black;"/> <div style="text-align: center;">= 0 DOF</div>
---

- Equations other than energy balance:

(1)

(2)

(3)

(4)

- Extent of reaction:  $\xi =$

- Enthalpy table. Use the heat of reaction method. Note that the reference state for a reactive species must be the state of that species in the reaction for which  $\Delta H_r^{\circ}$  is known:

## Section 7: F&R, Ch. 9 (Energy Balances – III)

<b>References:</b>				
<b>Species</b>	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ / mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ / mol)
C <sub>3</sub> H <sub>8</sub> (g)	100			
O <sub>2</sub> (g)	$\dot{n}_o$			
N <sub>2</sub> (g)				
CO <sub>2</sub> (g)				
H <sub>2</sub> O(v)				

Fill in molar quantities from the flow chart, blank out cells when appropriate and enter known or tabulated values of specific enthalpies, and label unknown specific enthalpies.

- **Q:** Why can't you use Table B.8 for outlet enthalpies? **A:** \_\_\_\_\_
- Energy balance. Fill in quantities from the enthalpy table along with the values of  $\xi$  and the standard heat of reaction.

(5)

- Expressions for unknown enthalpies. Carry out integrations but don't do any numerical calculations. Note that the heat of vaporization of water at 25°C is given in Equation 9.6-2a as 44.01 kJ/mol.

(6)

## Section 7: F&R, Ch. 9 (Energy Balances – III)

- The expressions for the specific enthalpies can be substituted into the energy balance [Eq. (5)], which can then be solved simultaneously with Eqs. (1) – (4) for  $T$  and the other unknown variables on the flow chart. (Also see Examples 9.5-3 and 9.5-4.)

### Thought Question:

Suppose you had a perfectly insulated gas grill that burns propane. The  $\Delta H$  between the feed (propane and air at room temperature) and the outlet ( $\text{CO}_2$  and water) is zero at steady state. How is that possible if the reaction is exothermic?

### Solution thermochemistry (Section 9.5c)

We showed in Section 8.5 that considerable energy can be released when some gases and solids dissolve in liquid solvents and when certain liquids (such as strong acids and water) are mixed together. In the same way, large heats of reaction may be associated with reactions between certain solutions, most notably acid solutions reacting with basic solutions.

- Eq. (9.5-3) defines the *standard heat of formation of a solution* as the sum of the enthalpy changes for forming a mole of the solute from its elements and then dissolving the solute in a specified number of moles (or an infinite amount) of the solvent. The units are  $\text{kJ/mol solute}$  (not per mole of solution).
- The standard heat of a reaction between solutions can be calculated from the standard heats of formation of the reactant and product solutions from Eq. (9.3-1). The procedure is illustrated in the paragraphs below Eq. (9.5-3) in the text and in Example 9.5-5.
- When you have a reaction between solutions and temperature changes are involved, the calculations can be tricky because the standard heat of reaction is expressed per mole of solute, while the heat capacity is more likely to be per mole of solution. You just need to keep track of how many moles of each are involved, and make sure you multiply each specific enthalpy change by the appropriate quantity. Example 9.5-6 illustrates the procedure. Try to follow it—it's long, but each step is straightforward.

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### Fuels and Combustion (Section 9.6)

A number of new terms are defined in this section, but the material and energy balance calculations are no different than the ones you've done up to now. Here's what you need to know.

- **Heating value of a fuel** (Section 9.6a). The negative of the standard heat of combustion of the fuel (so that it would be positive). The *higher heating value* presumes liquid water as one of the combustion products, and the *lower heating value* presumes water vapor. Eq. (9.6-1) gives the relationship between the two values (which you should be able to derive), and Eqs. (9.6-2a) and (9.6-2b) give the heat of vaporization of water at 25°C (which is needed to calculate a higher heating value from a lower heating value or vice versa). *See Example 9.6-1 and the Test Yourself on p. 521.*
- **Adiabatic flame temperature** (Section 9.6b). The temperature that would be attained in a combustion furnace if the reactor is adiabatic and combustion is complete—which is to say, the maximum temperature that can be achieved for the given inlet conditions. Example 3 on pp. 7-19 and 7-20 of this handout illustrates the calculation of an adiabatic flame temperature, as does Example 9.6-2. *Note that APEx is ideally suited to this calculation, which requires trial-and-error solution if a manual method is used.*
- **Flammability and ignition** (Section 9.6c) and **flames and detonations** (Section 9.6d). These sections consist entirely of definitions and explanations of phenomena that come up in both engineering practice and everyday life (e.g., what is a flame?). Learning them equips you to impress your friends and loved ones by being able to explain them, and also helps you avoid the embarrassment of being an engineer and not knowing how to explain them if someone asks you. You should be able to explain the difference between oxidation and combustion (burning), the concepts of ignition and autoignition temperature, the lower and upper flammability limits and explosive range of a fuel, a flame (exactly what is it?), flame velocity, stationary flame, and flashback, the difference between a blue flame and a yellow flame, and detonations and shock waves.

If you reached the last page of the coursepack (or wherever your instructor stopped for the semester), then it's time to celebrate! Look back at the early chapters – those things you might have struggled with initially (drawing the flowchart, labeling the flowchart, degree of freedom analysis, writing a material balance equation) should be second nature to you now. You're comfortable with reading what looks like a complicated word problem, translating it into a diagram, and translating that diagram into equations, which you can then solve to get the requested information. You look at the world differently now because you connect it to things you've learned in this course – mass balances, vapor-liquid equilibria, phase changes, energy balances, colligative properties, and others. (Just think of all the interesting tidbits you can drop at family dinners or student parties!) As you proceed to future engineering courses, you'll go into more detail about things you've learned here, and you'll start to challenge some of the assumptions that we've made about systems being ideal or at steady state. Each engineering course you take will serve as the foundation for the next one, and you'll find that you will continue to build on this material in future courses. Enjoy the rest of the journey!

