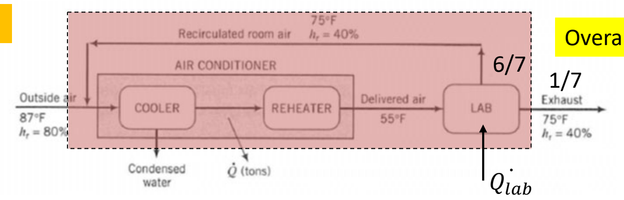
Prob 25-3b

Overall mass balance

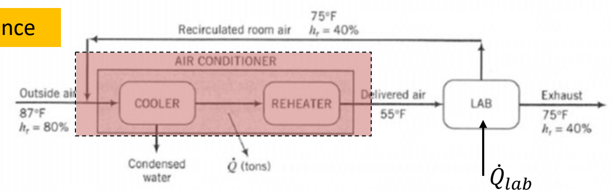


- “Delivered air” flow rate stays the same, but 6/7 is recycled

$$\dot{m}_{in,recycle} = \frac{1}{7}\dot{m}_{in,no\,recycle}$$

$$\dot{m}_{out,recycle} = \frac{1}{7}\dot{m}_{out,no\,recycle}$$

Heat balance



$$Q_{recycle} \neq \frac{1}{7}Q_{no\,recycle}$$

$$\dot{Q}_{recycle} = \Delta\dot{H} = \left(\sum \dot{m}_i \hat{H}_i\right)_{out} - \left(\sum \dot{m}_i \hat{H}_i\right)_{in}$$

$$\dot{Q}_{recycle} = \dot{m}_{H_2O,liq}\hat{H}_{H_2O,liq} + \dot{m}_{delivered\ air}\hat{H}_{delivered\ air} - \dot{m}_{inlet\ air}\hat{H}_{inlet\ air} - \dot{m}_{recycled\ air}\hat{H}_{recycled\ air}$$

We could also get $\dot{Q}_{lab}$

What was the purpose of Problem 25.3?

- Practice the following concepts:
  - Energy balances
  - Mass balances
  - Psychrometric chart
  - Recycle
  - Dry air as a constant quantity in balances

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Schedule

- Today – Heats of Reaction,
  Heat of Combustion
- Mon – Energy Balance with Reaction
  - **WARNING on Reading:**
    Skip "Heat of Reaction Method" on pages 505-506
    (450-451 in 3rd Ed.)
    Skip Examples 9.5-1, 9.5-2, and 9.5-3 (equations are generally wrong except in special circumstances!)
- Wed – Practice Energy Balance with Reaction
- Fri – Solid fuels
- Mon – Adiabatic Flame Temperature
- Wed – Transient Balances
- Fri before Thanksgiving – Review for Exam 3 & hand out exam
- Exam 3 due on Tuesday, Nov. 22

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Heat Capacity Table

- I have put an Excel spreadsheet on my web page with all of the heat capacity info for the HW
- This is meant to reduce time and prevent errors of typing in numbers

Level 3 Competency Exam

- See list of competencies
  - Show how many are from the ChE 273 class
- See booklet
- Also on ChE web page
  - Undergraduate page

Heats of Reaction
1. Definition

- ΔH_r = heat of reaction (kJ/mol or Btu/lbmol or cal/mol)
  - If $\Delta H_r < 0$, exothermic (gives off heat)
  - If $\Delta H_r > 0$, endothermic (needs heat)
- ΔH_r^0 = standard heat of reaction (i.e., at 25°C)
- Heat of reaction always defined by complete reaction (i.e., when $X_A = 1$) even if the reaction does not go to completion
  - Heat absorbed **per mole reacted for a given reactant**
- Remember for a single reaction, $\xi = \frac{n_{A,out} - n_{A,in}}{\nu_A} = \frac{n_{A,reacted}}{\nu_A}$
- Therefore $\Delta H_{system} = \xi \, \Delta H_r$

$$(moles\ reacted) \cdot \left(\frac{kJ\ of\ energy}{moles\ reacted}\right)$$

Why are Heats of Reaction Important?

- Exothermic Reactions
  - Must be controlled
  - May lead to runaway conditions
    - See video
- Endothermic Reactions
  - Must be controlled
  - Incomplete conversion if T drops too low

Heats of Reaction
2a. From Heats of Formation

- ΔH_f^0 = heat required to form species at 1 atm, 25°C
  - Tabulated in Table B.1, 2nd to last column
  - Assumes all reactants and products at 25°C
- $\Delta H_r^0 = \sum \nu_i \Delta H_{f,i}^0$
  - Remember negative sign for reactants
  - Like products minus reactants
  - Usually per mole of one of the reactants (must specify!)
- Example: Gasification of carbon

$$C(s) + H_2O(g) \Rightarrow CO(g) + H_2(g)$$

Species	ν_i	$\Delta H_{f,i}^0$ (kJ/mol)
C(s)	-1	0.0
H_2O	-1	-241.83
CO	1	-110.52
H_2	1	0.0

ΔH_r^0 = -110.52 + 0 – 0 – (-241.83) = +131.31 kJ/mol

CO H_2 C(s) $H_2O(g)$

Endothermic!
(products have more energy than reactants,
so energy has to be supplied)

Heats of Reaction
2b. Another example

- Example: Find the heat of reaction for partial oxidation of propane

$$C_3H_8 + 3O_2(g) \Rightarrow 3CO(g) + H_2(g) + 3H_2O(g)$$

Species	ν_i	$\Delta H_{f,i}^0$ (kJ/mol)
C_3H_8	-1	-103.8
O_2	-3	0.0
CO	3	-110.52
H_2	1	0.0
$H_2O(g)$	3	-241.83

See spreadsheet

ΔH_r^0 = (3)*(-110.52) + (1)*(0) + (3)*(-241.83) + (-1)*(-103.8) +(-3)*(0.0)= -953.25 kJ/mol

CO H_2 H_2O C_3H_8 O_2

Exothermic!

Note that this Heat of Reaction is per mole of C_3H_8 reacted (not per mole of O_2)!

Heats of Reaction
3. Path Independent

- $C(s) + O_2 \Rightarrow CO_2$ ΔH_r^0 = -393.51 kJ/mol

- $C(s) + \frac{1}{2}O_2 \Rightarrow CO$ ΔH_r^0 = -110.52 kJ/mol
- $\underline{CO + \frac{1}{2}O_2 \Rightarrow CO_2}$ $\underline{\Delta H_r^0 = -282.99 \text{ kJ/mol}}$
- $C(s) + O_2 \Rightarrow CO_2$ ΔH_r^0 = -393.51 kJ/mol

- Hess's Law:
  - Add or subtract reactions to get correct ΔH_r

Heats of Reaction
4. Heat of Combustion

- ΔH_c^0 = heat of combustion at 1 atm, 25°C
  - Tabulated in Table B.1, Last last column
  - Assumes all reactants and products at 25°C
  - All C $\Rightarrow$ CO_2 (g)
  - All H $\Rightarrow$ H_2O (liq) (for "high heating value")
  - All S $\Rightarrow$ SO_2 (g)
  - All N $\Rightarrow$ N_2 (g)
- Heating value = - ΔH_c^0
- Same as heat of reaction, assuming the species above
- Example: $NH_3 + \frac{3}{4} O_2 \Rightarrow 3/2\ H_2O(liq) + \frac{1}{2} N_2$

$\Delta H_{f,i}^0$ (kJ/mol):	-46.19	0.0	-285.84	0.0

ΔH_r = (3/2)*(-285.84) – (-46.19) = -382.57 kJ/mol

(same as ΔH_c^0 in Table B.1)

Heats of Reaction
5. ΔH_r at Different Temperatures

Review:

- How do you find $\widehat{H}$ at different temperatures?

$$\widehat{H} = \Delta\widehat{H}_f^0 + \int_{25^\circ\mathrm{C}}^{T} \hat{C}_p \, dT$$

- Suppose $\hat{C}_{p,methane} \approx 0.079 \frac{kJ}{mol\,^\circ\mathrm{C}}$
  and $\Delta\widehat{H}_{f,methane}^0 = -74.85 \frac{kJ}{mol}$
- Find $\widehat{H}_{methane}$ at 400°C
- $\widehat{H} = -74.85 \frac{kJ}{mol} + \int_{25^\circ\mathrm{C}}^{400^\circ\mathrm{C}} 0.079 \frac{kJ}{mol\,^\circ\mathrm{C}} dT$

$$= -74.85 + 0.079 * (400 - 25) = -45.22 \frac{\mathrm{kJ}}{\mathrm{mol\ CH_4}}$$

Multiple Species

- Calculate the energy required to raise a mixture from 25°C to 400°C.

Species	Gram-moles
O_2	0.05
CO_2	1.0
H_2O	0.3

$$\Delta H = \sum n_i \Delta H_i$$

$$\Delta H_{O2} = \int_{25}^{400} C_{p,O_2} dT$$

$$= a_{O_2}(400 - 25) + \frac{b_{O_2}}{2}(400^2 - 25^2) + \frac{c_{O_2}}{3}(400^3 - 25^3)$$

$$+ \frac{d_{O_2}}{4}(400^4 - 25^4)$$

Multiple Species

- Now get $\Delta H = \sum n_i \Delta H_i$

$$0.05 * \left(a_{O_2}(400-25) + \frac{b_{O_2}}{2}(400^2-25^2) + \frac{c_{O_2}}{3}(400^3-25^3) + \frac{d_{O_2}}{4}(400^4-25^4) \right)$$

$$1.0 * \left(a_{CO_2}(400-25) + \frac{b_{CO_2}}{2}(400^2-25^2) + \frac{c_{CO_2}}{3}(400^3-25^3) + \frac{d_{CO_2}}{4}(400^4-25^4) \right)$$

$$0.30 * \left(a_{H_2O}(400-25) + \frac{b_{H_2O}}{2}(400^2-25^2) + \frac{c_{H_2O}}{3}(400^3-25^3) + \frac{d_{H_2O}}{4}(400^4-25^4) \right)$$

This is a lot of programming or punching buttons on a calculator!

Shortcut
(Combine coefficients)

$$0.05 * \left(a_{O_2}(400-25) + \frac{b_{O_2}}{2}(400^2-25^2) + \frac{c_{O_2}}{3}(400^3-25^3) + \frac{d_{O_2}}{4}(400^4-25^4) \right)$$

$$1.0 * \left(a_{CO_2}(400-25) + \frac{b_{CO_2}}{2}(400^2-25^2) + \frac{c_{CO_2}}{3}(400^3-25^3) + \frac{d_{CO_2}}{4}(400^4-25^4) \right)$$

$$0.30 * \left(a_{H_2O}(400-25) + \frac{b_{H_2O}}{2}(400^2-25^2) + \frac{c_{H_2O}}{3}(400^3-25^3) + \frac{d_{H_2O}}{4}(400^4-25^4) \right)$$

Define new variables:

$a' = \sum n_i a_i \qquad b' = \sum n_i b_i \qquad c' = \sum n_i c_i \qquad d' = \sum n_i d_i$

Now ΔH becomes:

$$\boxed{\Delta H = a'(400-25) + \frac{b'}{2}(400^2-25^2) + \frac{c'}{3}(400^3-25^3) + \frac{d'}{4}(400^4-25^4)}$$

If this approach is confusing, don't use this shortcut method

Two Methods to Find ΔH_{rxn} as f(T)

- Path Method (A→B)

$$\begin{tikzcd}
A \arrow[r, "\Delta H_r \text{ at } T"] \arrow[d, dashed] & B \\
A \text{ at } 25°C \arrow[r, dashed, "\Delta H_r \text{ at } 25°C"] & B \text{ at } 25°C \arrow[u, dashed]
\end{tikzcd}$$

$$\Delta H_T = \int_{T}^{25\,C} C_{p,A}dT + \Delta H_{r,25\,C} + \int_{25}^{T} C_{p,B}\,dT$$

- Heat of Formation

$$\hat{H}_i = \Delta\hat{H}^0_{f,i} + \int_{25}^{T} C_{p,i}\,dT$$

$$\Delta\hat{H}_{rxn} = \sum v_i\hat{H}_i$$

or

$$\Delta\hat{H}_{rxn} = \left(\sum n_i\hat{H}_i\right)_{out} - \left(\sum n_i\hat{H}_i\right)_{in}$$

Example

- $CO + ½\,O_2 \rightarrow CO_2$
- Find the heat of reaction at 1200°C
  A. Path method
  B. H_{out} - H_{in} (ΔH_f^0 approach)

Need volunteer for spreadsheet

HW

- Practice finding heat of reaction
- Find the heat of reaction at elevated temperature
  A. Path method
  B. H_{out} - H_{in} (ΔH_f^0 approach)
- Work the first problem on the Case Study with your team