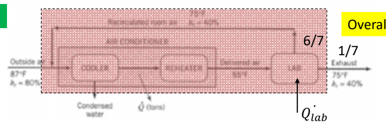
Prob 8-88b

Prob 8-74b 3rd Ed.

Overall mass balance

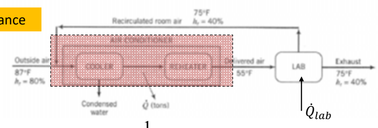


- "Delivered air" flow rate stays the same, but 6/7 is recycled

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

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

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 8.88?

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

Schedule

- Today – Heats of Reaction,
  Heat of Combustion
- Wed – 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!)
- Fri – Practice Energy Balance with Reaction
- Mon – Adiabatic Flame Temperature
- Tues – Transient Balances
- Mon after Thanksgiving – Review for Exam 3

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., $X_A = 1$) even if the reaction does not go to completion
  - Heat absorbed **per mole reacted**
- Remember for a single reaction, $\xi = \frac{n_{A,out} - n_{A,in}}{\nu_A} = \frac{n_{A,reacted}}{\nu_A}$
- Therefore $\Delta H_{system} = \xi\,\Delta H_r$

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

Heats of Reaction
2. From Heats of Reaction

- 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
- 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

Endothermic!

Heats of Reaction
3. Path Independent

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

- C(s) + ½$O_2 \Rightarrow$ CO ΔH_r^0 = -110.52 kJ/mol
- CO + ½$O_2 \Rightarrow CO_2$ ΔH_r^0 = -282.99 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, 2nd to 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
- Example: NH_3 + ¾ $O_2 \Rightarrow$ 3/2 H_2O(liq) + ½ 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
6. Review

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

$$\hat{H} = \Delta\hat{H}_f^0 + \int_{25°C}^{T} \hat{C}_p dT$$

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

$$= -74.85 + 0.079 * (400 - 25) = -45.22 \frac{\text{kJ}}{\text{mol CH}_4}$$

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
HO	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:

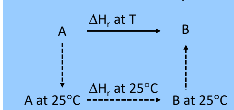
$a' = \sum n_i a_i$ $b' = \sum n_i b_i$ $c' = \sum n_i c_i$ $d' = \sum n_i d_i$

Now ΔH becomes:

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

Two Methods to Find ΔH_{rxn}

- Path Method (A→B)



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

$$\Delta C_p = a' + b'T + c'T^2 + d'T^3$$

$a' = \sum \nu_i a_i$, $b' = \sum \nu_i b_i$, etc.,
where ν_i is negative for reactants and positive for products

$$\Delta H_T = \Delta H_{r,25\,C} + \int_{25\,C}^{T} \Delta C_p dT$$
$$= \Delta H_{r,25\,C} + a'(T-25) + \frac{b'}{2}(T^2 - 25^2) + \frac{c'}{3}(T^3 - 25^3) + \frac{d'}{4}(T^4 - 25^4)$$

- Heat of Formation

$$\hat{H}_i = \Delta\hat{H}_{i,f}{}^o + \int_{T_{ref}}^{T} \hat{C}_p dT$$

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

or

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

See Excel Sheet

Example

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

See spreadsheet