CH365 Chemical Engineering Thermodynamics

Lesson 19
Heat Effects of Industrial Reactions

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Industrial Reactions

- Rarely carried out under standard conditions
- Reactants not in stoichiometric proportions
- Reaction may not go to completion
- Final T may differ from initial T
- Presence of inerts
- Multiple reactions

Review of Lesson 18

$$\Delta H^o = \Delta H^o_{298} + R \cdot \int_{T0}^{T} \frac{\Delta C^o_P}{R} dT = \Delta H^o_{298} + R \cdot IDCPH$$ Eq. 4.19

$$IDCPH = \int_{T_0}^{T} \frac{\Delta C^o_p}{R} dT = (\Delta A) \cdot (T - T_0) + \frac{\Delta B}{2} \cdot (T^2 - T_0^2) + \frac{\Delta C}{3} \cdot (T^3 - T_0^3) + \Delta D \cdot \left(\frac{T - T_0}{T \cdot T_0} \right)$$ Eq. 4.20

$$\Delta A = \sum_i \nu_i \cdot A_i, \quad \Delta B = \sum_i \nu_i \cdot B_i, \quad \text{etc.}$$

This only works when T is the same for reactants and products. (see L18 Slide 5) Not explained in book!

$$\Delta H^o = \Delta H^o_{298} + R \cdot \int_{T0}^{T} \frac{\Delta C^o_P}{R} dT = \Delta H^o_{298} + R \cdot MDCPH \cdot (T - T_0)$$ Eq. 4.22

$$MDCPH = \frac{\langle \Delta C^o_p \rangle_H}{R} = \Delta A + \frac{\Delta B}{2} \cdot (T + T_0) + \frac{\Delta C}{3} \cdot (T^2 + T_0^2 + T \cdot T_0) + \frac{\Delta D}{T \cdot T_0}$$ Eq. 4.21

$$\int_{T_0}^{T} \frac{\Delta C^o_p}{R} dT = IDCPH(T_0, T, DA, DB, DC, DD)$$

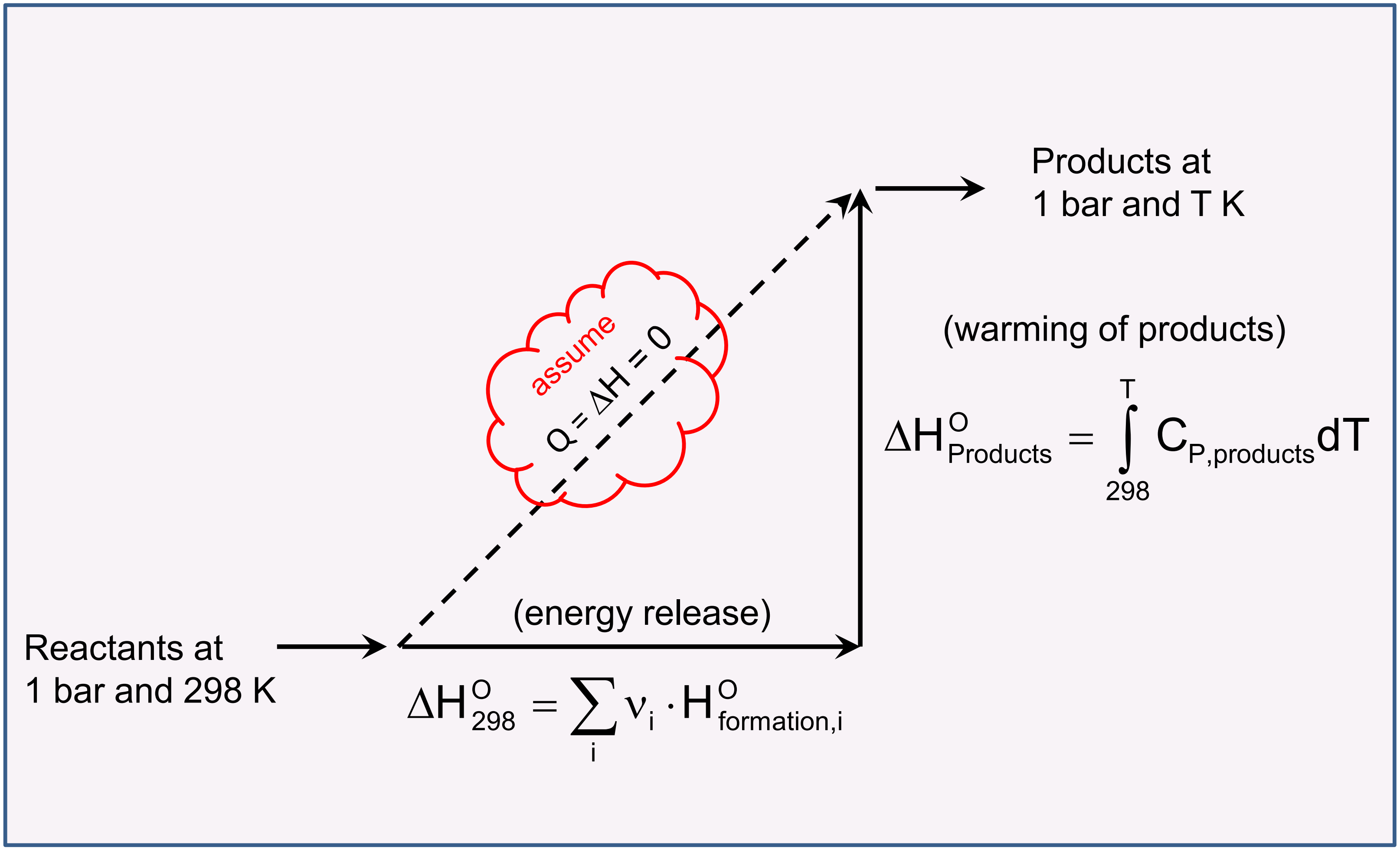
Functional nomenclature used in book

$$\frac{\langle \Delta C^o_p \rangle_H}{R} = MDCPH(\underbrace{T_0, T, DA, DB, DC, DD}_{\text{These are “parameters;” all but } T_0 \text{ change}})$$

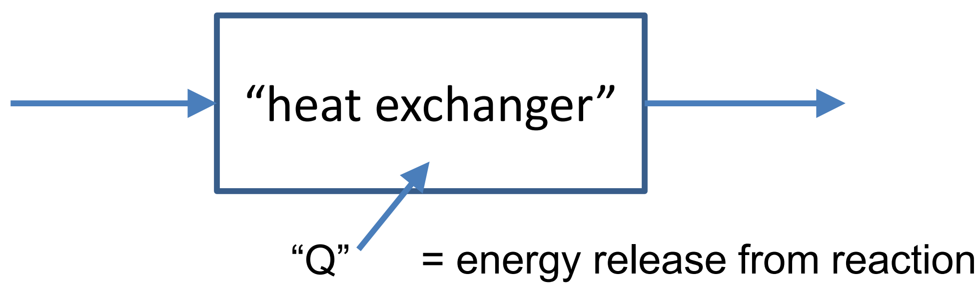
Example 4.7

What is the maximum temperature that can be reached by the combustion of methane with 20% excess air? Methane and air enter the burner at 25 deg C.

Important Example. “Adiabatic Flame Temperature”



Similar to
“nonadiabatic”
exchanger



Example 4.7

What is the maximum temperature that can be reached by the combustion of methane with 20% excess air? Methane and air enter the burner at 25 deg C.

Solution:

Part (2) - Mathematica

Part (1) Calculate heat of reaction at 298:

Balance:

$$CH_4(g) + 2\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g)$$

Add 20% excess O_2:

$$CH_4(g) + 2.4\,O_2(g) \rightarrow CO_2(g) + 2\,H_2O(g) + 0.4\,O_2(g)$$

Add N_2:

$$N_2 \text{ in feed} = (O_2 \text{ in feed}) \cdot \frac{79}{21} = 2.4 \cdot \frac{79}{21} = 9.03 \text{ moles}$$

Actual: $CH_4(g) + 2.4\,O_2(g) + 9.03\,N_2(g) \rightarrow CO_2(g) + 2\,H_2O(g) + 0.4\,O_2(g) + 9.03\,N_2(g)$

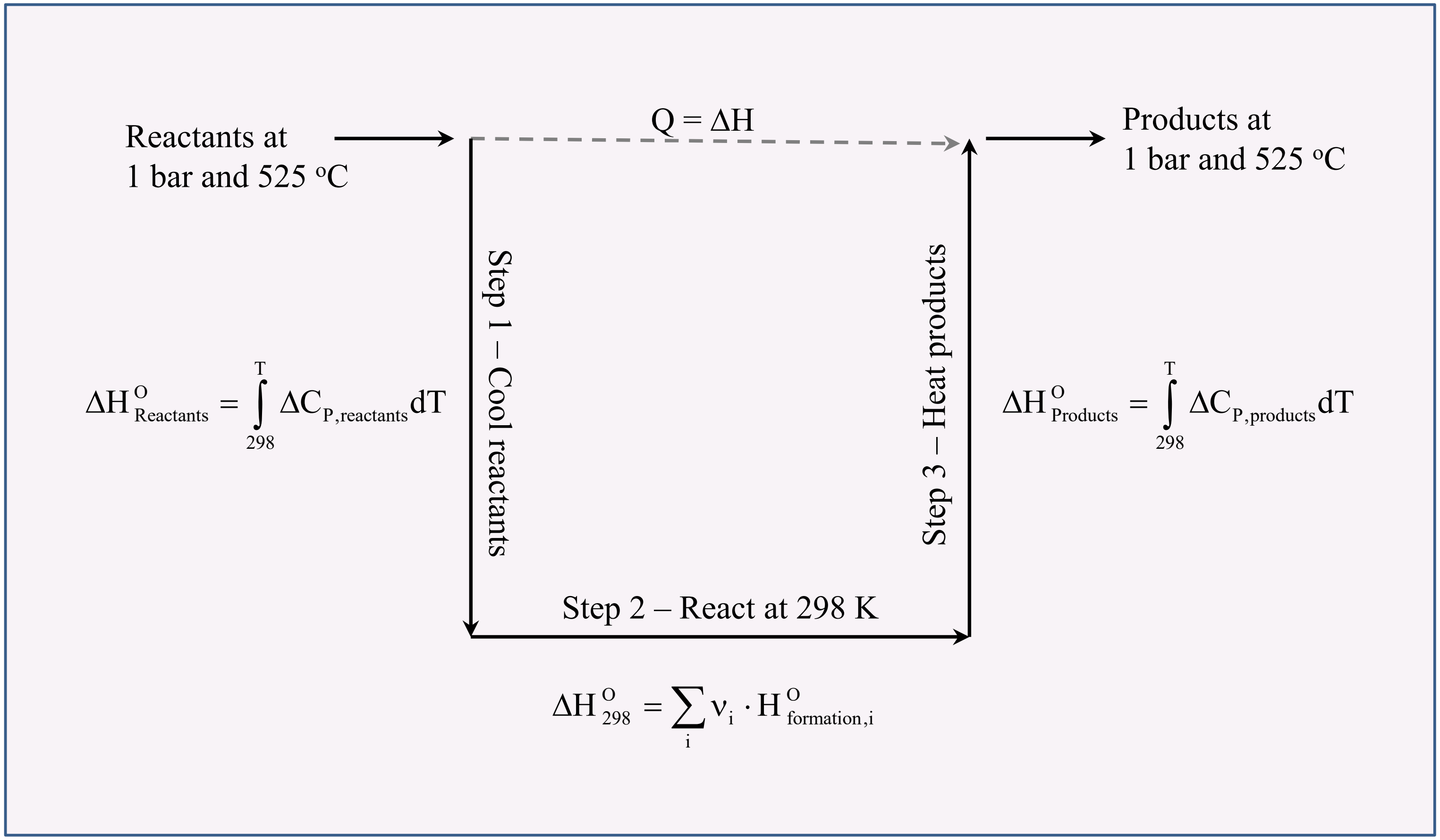
Homework

Problem 4.45

A process for the production of 1,3-butadiene results from the catalytic dehydrogenation at atmospheric pressure of 1-butene according to the reaction:

$$C_4H_8\ (g) \rightarrow C_4H_6\ (g) + H_2\ (g)$$

To suppress side reactions, the 1-butene feed is diluted with steam in the ratio of 10 moles of steam per mole of 1-butene. The reaction is carried out *isothermally* at 525 deg C, and at this temperature 33% of the 1-butene is converted to 1,3-butadiene. How much heat is transferred to the reactor per mole of entering 1-butene?



Thermal process for problem 4.45

Problem 4.55

A natural-gas fuel contains 85mol-% methane, 10 mol-% ethane, and 5 mol-% nitrogen.

(a) What is the standard heat of combustion (kJ/mol) of the fuel at 25 deg C with $H_2O(g)$ is a product?

(b) The fuel is supplied to a furnace with 50% excess air, both entering at 25 deg C. The products leave at 600 deg C. If combustion is complete and if no side reactions occur, how much heat (kJ per mole of fuel) is transferred in the furnace?

Must find a balanced chemical equation:

All species are gas-phase.
Strategy - The reaction is built up in steps to show where each coefficient comes from.

Step 1 - Balance the reactions:

$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$

$C_2H_6 + \frac{7}{2}\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$

Step 2 - Multiply the reactions by the feed composition:

$0.85\ [CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O]$

$0.10\ [C_2H_6 + \frac{7}{2}\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O]$

Step 3 - Add the reactions:

$0.85\ CH_4 + 1.70\ O_2 \rightarrow 0.85\ CO_2 + 1.70\ H_2O$

$0.10\ C_2H_6 + 0.35\ O_2 \rightarrow 0.20\ CO_2 + 0.30\ H_2O$

$0.85\ CH_4 + 0.10\ C_2H_6 + 2.05\ O_2 \rightarrow 1.05\ CO_2 + 2.00\ H_2O$

Step 4 - Add the **0.05 N_2** that comes in with the natural gas::

$0.85\ CH_4 + 0.10\ C_2H_6 + 2.05\ O_2 + \mathbf{0.05\ N_2} \rightarrow 1.05\ CO_2 + 2.00\ H_2O + \mathbf{0.05\ N_2}$

Step 5 - Add the nitrogen that enters with the air (2.05 x 79/21 = **7.712 N_2**):

$0.85\ CH_4 + 0.10\ C_2H_6 + 2.05\ O_2 + \mathbf{0.05\ N_2} + \mathbf{7.712\ N_2} \rightarrow 1.05\ CO_2 + 2.00\ H_2O + \mathbf{0.05\ N_2} + \mathbf{7.712\ N_2}$

Step 6 - Add the excess air (2.05 x 0.5 = **1.025 O_2** and 7.712 x 0.5 = **3.856 N_2**):

$0.85\ CH_4 + 0.10\ C_2H_6 + 2.05\ O_2 + \mathbf{1.025\ O_2} + \mathbf{0.05\ N_2} + \mathbf{7.712\ N_2} + \mathbf{3.856\ N_2}$

$\rightarrow 1.05\ CO_2 + 2.00\ H_2O + \mathbf{1.025\ O_2} + \mathbf{0.05\ N_2} + \mathbf{7.712\ N_2} + \mathbf{3.856\ N_2}$

Step 7 - Combine common species (all species are gas phase):

$0.85\ CH_4 + 0.10\ C_2H_6 + 3.075\ O_2 + 11.618\ N_2 \rightarrow 1.05\ CO_2 + 2.00\ H_2O + 1.025\ O_2 + 11.618\ N_2$