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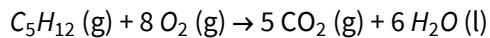
## Problem Set 7 - Solutions

### Problem 4.22

What is the standard heat of combustion of n-pentane gas at 25 °C if the combustion products are  $H_2O(l)$  and  $CO_2(g)$ ?

#### Solution

Balanced Reaction:



$$\nu = \{-1, -8, 5, 6\};$$

$$\Delta Hf298 = \{-146\ 760, 0, -393\ 509, -285\ 830\}; (*J/mol*)$$

$$\Delta H298 = \text{Plus @@ } (\nu * \Delta Hf298)$$

Out[ ]=

$$-3\ 535\ 765$$

(\*J per mole n-pentane\*)

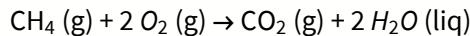
The standard heat of combustion of n-pentane gas at 25 °C with products  $H_2O(l)$  and  $CO_2(g)$  is -3,535,765 J per mol of n-pentane. //ANS

## Problem 4.28

Natural gas (assume pure methane) is delivered to a city via pipeline at a volumetric rate of 150 million standard cubic feet per day. If the selling price of the gas is \$5.00 per GJ of higher heating value, what is the expected revenue in dollars per day? Standard conditions are 60 °F and 1 atm.

### Solution

Balanced combustion reaction:



$$\begin{aligned} \nu &= \{-1, -2, 1, 2\}; \\ \Delta H_f^{298} &= \{-74520, 0, -393509, -285830\}; (*\text{J/mol*}) \\ \Delta H^{298} &= \text{Plus @@ } (\nu * \Delta H_f^{298}) (*\text{HHV*}) \end{aligned}$$

Out[ ] =

$$-890649$$

$$(*n=P*V/R*T*)$$

$$R = 0.7302 * \frac{\text{ft}^3 \text{ atm}}{\text{lbmol} * \text{degR}};$$

$$T = (60 + 459.67) * \text{degR};$$

$$n = \frac{150000000 * \frac{\text{ft}^3}{\text{d}} * 1 \text{ atm}}{R * T} * \frac{1000 \text{ gmol}}{2.20462 \text{ lbmol}}$$

Out[ ] =

$$\frac{1.793032 \times 10^8 \text{ gmol}}{\text{d}}$$

Convert gram-moles to GJ and the GJ to dollars:

$$\frac{n \text{ gmol}}{\text{d}} * \frac{\text{Abs} [\Delta H^{298}] \text{ J}}{\text{gmol}} * \frac{1 \text{ GJ}}{10^9 \text{ J}} * \frac{5 \text{ dollars}}{\text{GJ}}$$

Out[ ] =

$$\frac{798481.1 \text{ dollars gmol}}{\text{d}^2}$$

The expected revenue is \$798,481.10 per day. //ANS

## Problem 4.53

Saturated water vapor, i.e., *steam*, is commonly used as a heat source in heat exchanger applications. Why *saturated* water vapor? Why saturated *water vapor*?

In a plant of any reasonable size, several varieties of saturated steam are commonly available. For example, saturated steam may be available at 4.5, 9, 17, and 33 bar. But the higher the pressure, the lower the useful energy content and the greater the cost. Why is the energy content lower at higher pressure? Why then is higher-pressure steam used?

### Solution

*Saturated* vapor is used because latent heat  $\Delta H_{lv}$  is large compared to sensible heat. As a result, latent heat will overwhelm sensible heat in enthalpy calculations. //ANS

Water is used because it is cheap, readily available, non-toxic, and has a large  $\Delta H_{lv}$ . //ANS

Steam is lower at higher pressure is at a higher temperature because the steam molar volume decreases as pressure is increased, as can be seen in the ideal gas equation  $PV=RT$ . From the Clapeyron equation (equation 6.85, page 252), where  $T_{lv}$  is the temperature of the phase transition, with  $\Delta V_{lv} \sim V_v$  (vapor) because the liquid volume is relatively small, and noting that  $dP^{\text{sat}}/dt$  is unaffected by total pressure, we see that  $\Delta H_{lv}$  is roughly proportional to  $V$ :

Out[•]//TraditionalForm=

$$\Delta H_{lv} = T_{lv} \Delta V_{lv} \frac{dP^{\text{sat}}}{dT}$$

Out[•]//TraditionalForm=

$$\Delta H_{lv} \approx T_{lv} V_v \text{ const}$$

Note that  $T_{lv}$  increases with pressure and  $V_v$  decreases. Assuming that as pressure increases,  $V_v$  decreases faster than  $T_{lv}$  increases, the lower energy content at higher pressure is a result of the decrease in  $\Delta H_{lv}$  should increase with pressure. //ANS

Students can also use Google AI to answer this question since we have not yet covered this in class (lesson 31). Search “How does heat of vaporization depend on pressure?”

High-pressure steam is used because higher pressures allow higher temperatures. //ANS

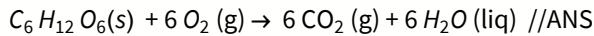
## Problem 4.54

The oxidation of glucose provides the principal source of energy for animal cells. Assuming the reactants are glucose [ $C_6 H_{12} O_6(s)$ ] and oxygen [ $O_2(g)$ ] and the products are  $CO_2(g)$  and  $H_2 O(l)$ , answer the following:

- Write a balanced equation for glucose oxidation, and determine the standard heat of reaction at 298 K.
- During a day, an average person consumes about 150 kJ of energy per kg of body mass. Assuming glucose is the only source of energy, estimate the mass (grams) of glucose required daily to sustain a person of 57 kg.
- For a population of 275 million people, what mass of  $CO_2$  (a greenhouse gas) is produced daily by mere respiration? Data: for glucose,  $\Delta H_{f,298}^\circ = -1,274.4 \text{ kJ/mol}$ . Ignore the effect of temperature on the heat of reaction.

### Solution - Part (a)

Balanced oxidation (combustion) reaction:



Standard heat of reaction at 298K:

$$\begin{aligned} v &= \{-1, -6, 6, 6\}; \\ \Delta H_{f,298} &= \{-1274.4, 0, -393509 / 1000, -285830 / 1000\}; \\ \Delta H_{rxn} &= \text{Plus @@}(v * \Delta H_{f,298}) \end{aligned}$$

*Out[ ] =*  
-2801.634

The standard heat of reaction at 298 K is -2,801.63 kJ per mole of glucose. //ANS

### Solution - Part (b)

Total energy consumption for a 57-kg person:

$$\frac{150 \text{ kJ}}{\text{kg}} * 57 \text{ kg}$$

*Out[ ] =*  
8550 kJ

Moles of glucose required:

$$\frac{8550 \text{ kJ}}{2801.63 \text{ kJ/mol}}$$

*Out[ ] =*  
3.051795 mol

Mass required:

molar mass of glucose »

D-(+)-glucose CHEMICAL [ molar mass ]

Out[°]=

$$180.16 \text{ g/mol}$$

The molar mass of glucose is 180.16 g/mol.

$$\frac{3.05 \text{ mol}}{\text{day}} * \frac{180.16 \text{ g}}{\text{mol}}$$

Out[°]=

$$\frac{549.488 \text{ g}}{\text{day}}$$

The 57-kg person requires about 550 g of glucose. //ANS

### Solution - Part (c)

molar mass of CO<sub>2</sub>

carbon dioxide CHEMICAL [ molar mass ]

Out[°]=

$$44.009 \text{ g/mol}$$

$$\frac{3.05 \text{ mol}}{\text{day}} * \frac{6 \text{ mol}}{1 \text{ mol}} * 275\,000\,000 * \frac{44 \text{ g}}{\text{mol}} * \frac{1 \text{ kg}}{1\,000 \text{ g}} * \frac{1 \text{ tonne}}{1\,000 \text{ kg}}$$

Out[°]=

$$\frac{221\,430. \text{ tonne}}{\text{day}}$$

221,430 metric tons of CO<sub>2</sub> are produced per day. //ANS

## 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:



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°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?

### Solution

This problem is an application of Equation 4.22 and follows Example 4.7 closely. A new balanced equation is implied to account for the water in the enthalpy integrals:



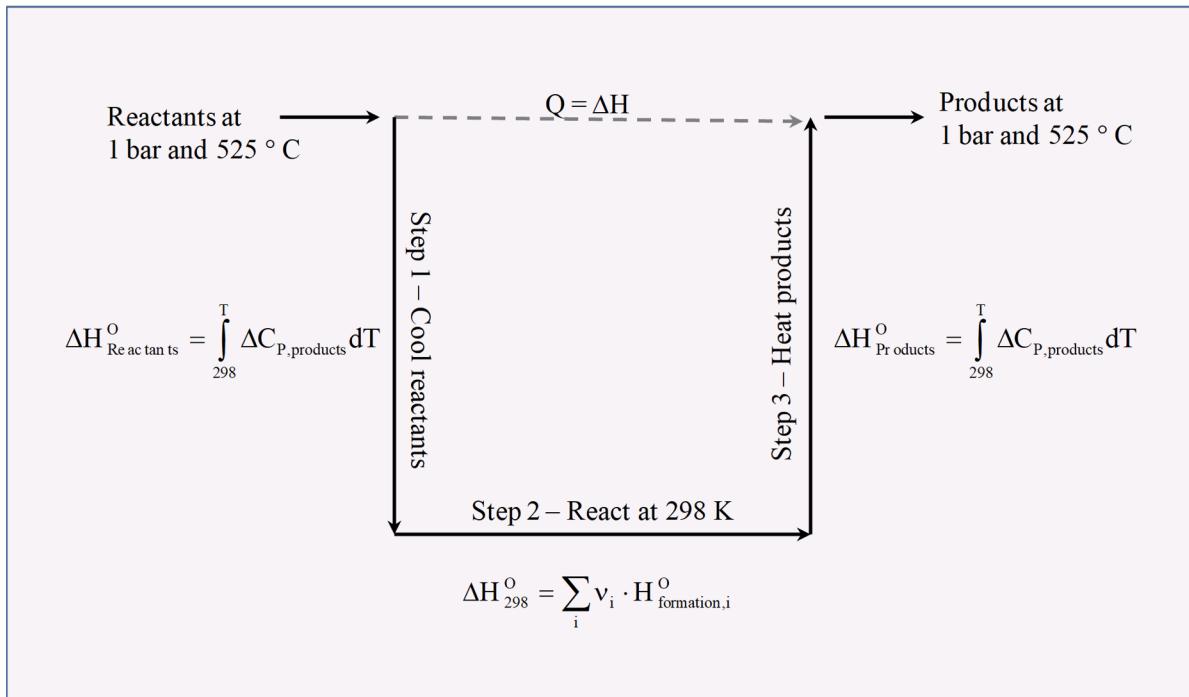
```
In[1]:= (*Stoichiometric coefficients*)
(*1-butene, water, 1,3-butadiene, hydrogen, water*)
v = {-1, -10, 1, 1, 10};

In[2]:= (*Standard Heats of Formation*)
(*1-butene,1,3-butadiene,hydrogen*)
ΔHf298 = {-540, -241818, 109240, 0.000, -241818};

(*Heat of Reaction at 298 K*)
ΔH298 = Plus @@ (v * ΔHf298) (*J/mol (J per mole of 1-butene)*)

Out[2]=
109780.
```

Assume that the reactants enter the process at 525°C. The process temperature diagram is shown below. The diagram shows the process broken down into three steps. In step 1, the reactants are cooled to 25°C because the standard heat of reaction is known at 25°C. In step 2, the reaction occurs at 25°C. In step 3, the products are heated back up to 525°C. Water as steam appears in steps 1 and 3 in the same amount, and does not really need to be included in the heat capacity polynomials. The same answer is obtained if water is not included. However, we will include it in this solution.



```
In[1]:= (*Heat Capacity polynomial coefficients, Table C.1:*)
(*1-butene, water, 1,3-butadiene, hydrogen, water*)
a = {1.967, 3.470, 2.734, 3.249, 3.470};
b = {31.630, 1.450, 26.786, 0.422, 1.450} * 10-3;
c = {-9.873, 0.000, -8.882, 0.000, 0.000} * 10-6;
d = {0.000, .121, 0.000, 0.083, 0.121} * 105;

In[2]:= (*Stoichiometric coefficients*)
(*1-butene, water, 1,3-butadiene, hydrogen, water*)
(*same as before - re-defined only if feed is at T0*)
v = {-1, -10, 1, 1, 10};

In[3]:= Δa = Plus @@ (v * a);
Δb = Plus @@ (v * b);
Δc = Plus @@ (v * c);
Δd = Plus @@ (v * d);

In[4]:= (*Temperatures, K*)
T = 798.15;
T0 = 298.15;

In[5]:= (*Gas constant*)
R = 8.314; (* $\frac{\text{J}}{\text{mol}\cdot\text{K}}$ *)

(*Equation 4.21 for MCPH*)
MCPH = Δa +  $\frac{\Delta b}{2} \cdot (T + T0)$  +  $\frac{\Delta c}{3} \cdot (T^2 + T0^2 + T \cdot T0)$  +  $\frac{\Delta d}{T \cdot T0}$ 

Out[5]= 1.945 369
```

(\*Equation 4.22 for corrected heat of reaction\*)  
(\*Gives molar heat of reaction in J/mol 1-butene\*)  
 $\Delta H_{798} = \Delta H_{298} + MCPH * R * (T - T_0)$

Out[8]=  
117866.9

(\*Heat requirement in J/mol 1-butene\*)  
 $Q = .33 * \Delta H_{798}$

Out[9]=  
38896.08

(\*//ANS\*)

Heat requirement is 38,896.1 J per mol 1-butene. //ANS

## Problem 4.55

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

- What is the standard heat of combustion (kJ/mol) of the fuel at 25°C with  $H_2O(g)$  as a product?
- The fuel is supplied to a furnace with 50% excess air, both entering at 25°C. The products leave at 600°C. If combustion is complete and if no side reactions occur, how much heat (kJ per mole of fuel) is transferred in the furnace?

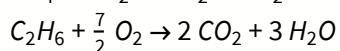
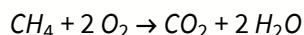
### Solution - Part (a)

Balanced Chemical Equations, assuming carbon dioxide and water as products

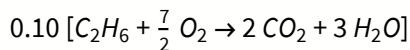
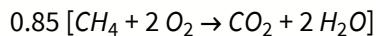
All species are gas-phase.

Strategy - The reaction is built up in steps to show where each coefficient comes from.

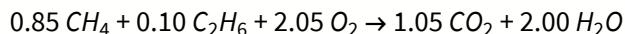
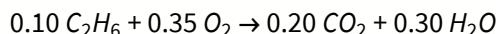
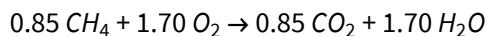
Step 1 - Balance the reactions:



Step 2 - Multiply the reactions by the feed composition:



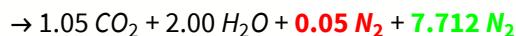
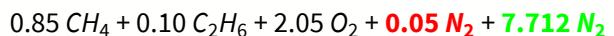
Step 3 - Add the reactions:



Step 4 - Add the **0.05 N<sub>2</sub>** that comes in with the natural gas::



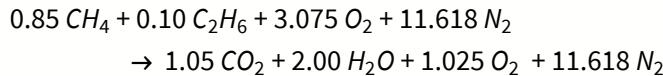
Step 5 - Add the nitrogen that enters with the air ( $2.05 \times 79/21 = \textcolor{green}{7.712 N}_2$ ):



Step 6 - Add the excess air ( $2.05 \times 0.5 = \textcolor{teal}{1.025 O}_2$  and  $7.712 \times 0.5 = \textcolor{teal}{3.856 N}_2$ ):



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



```
In[1]:= (*Stoichiometric coefficients*)
(*List order: methane, ethane, oxygen, nitrogen,
carbon dioxide, water, oxygen, nitrogen*)
v = {-0.85, -0.10, -3.075, -11.618, 1.05, 2.00, 1.025, 11.618};

In[2]:= (*Standard Heats of Formation at 298K*)
ΔHf298 = {-74520, -83820, 0.000, 0.000, -393509, -241818, 0.000, 0.000};

(*Standard Heat of Reaction at 298 K*)
ΔH298 = Plus @@ (v * ΔHf298) (*//ANS, J per mole of feed*)

Out[2]= -825096.5
```

## Solution - Part (b)

There is no heat requirement to warm or cool the reactants and we consider only the products in the application of Equation 4.20.

```
In[1]:= (*Stoichiometric coefficients of products*)
(*carbon dioxide, water, oxygen, nitrogen*)
v = {1.05, 2.00, 1.025, 11.618};

In[2]:= (*Heat Capacity polynomial coefficients of products*)
(*carbon dioxide, water, oxygen, nitrogen*)
a = {5.457, 3.470, 3.639, 3.280};
b = {1.045, 1.450, 0.506, .593} * 10^-3;
c = {0.000, 0.000, 0.000, 0.000} * 10^-6;
d = {-1.157, 0.121, -.227, 0.040} * 10^5;

In[3]:= Δa = Plus @@ (v * a);
Δb = Plus @@ (v * b);
Δc = Plus @@ (v * c);
Δd = Plus @@ (v * d);

In[4]:= (*Temperatures*)
T1 = 600 + 273.15;
T0 = 25 + 273.15;

In[5]:= (*Gas constant*)
R = 8.314; (*J/mol*K*)

(*Equation 4.21 for MDCPH*)
MDCPH = Δa + Δb/2 * (T1 + T0) + Δc/3 * (T1^2 + T0^2 + T1 * T0) + Δd/(T1 * T0)

Out[5]= 60.90186
```

(\*Use Equation 4.21 for corrected heat of reaction in J/mol\*)

$$\Delta H_{873} = \Delta H_{298} + MDCPH * R * (T_1 - T_0)$$

Out[ ]=

$$-533\,952.1$$

(\*Units are J/mol of natural gas feed \*)

$$(*Q=\Delta H_{798}=-533,952 \text{ J/mol}=-533.952 \text{ kJ/mol}*)$$

### Alternate Solution - Part (b) - using Eq. 4.19 for IDCPh

$$\ln[ ] := IDCPh = \Delta a * (T_1 - T_0) + \frac{\Delta b}{2} * (T_1^2 - T_0^2) + \frac{\Delta c}{3} * (T_1^3 - T_0^3) + \Delta d * \left( \frac{T_1 - T_0}{T_1 * T_0} \right);$$

$$\Delta H_{798} = \Delta H_{298} + IDCPh * R$$

Out[ ]=

$$-533\,952.1$$

(\*Units are J/mol of natural gas feed \*)

$$(*Q=\Delta H_{798}=-533,952 \text{ J/mol}=-533.952 \text{ kJ/mol}*)$$

## Problem 4.6

If the heat capacity of a substance is correctly represented by an equation of the form

$$C_P = A + BT + CT^2,$$

show that the error resulting when  $\langle C_P \rangle_H$  (MCPH) is assumed equal to  $C_P$  evaluated at the arithmetic mean of the initial and final temperatures is

$$C(T_2 - T_1)^2 / 12.$$

### Solution

```
In[1]:= Clear["Global`*"]

In[2]:= Cp[T_] = A + B*T + C*T^2;

(*Arithmetic mean temperature (average)*)
avgT = (T1 + T2)/2;

(*Cp evaluated at the average temperature*)
Cp[avgT]

Out[3]=
A + B (T1 + T2) + C (T1 + T2)^2/4

In[4]:= (*MCPH which is equal to <Cp>_H*)
MCPH = A + B/2 (T2 + T1) + C/3 (T2^2 + T1^2 + T2*T1)

Out[5]=
A + B (T1 + T2) + C (T1^2 + T1 T2 + T2^2)/3

In[6]:= (*Demonstration of the Expand function to see what it does.*)
Expand[Cp[avgT]]

Out[7]=
A + B T1/2 + C T1^2/4 + B T2/2 + C T1 T2/2 + C T2^2/4

In[8]:= Expand[MCPH]

Out[9]=
A + B T1/2 + C T1^2/3 + B T2/2 + C T1 T2/3 + C T2^2/3
```

Let the let error be given by the difference between the two expressions:

```
In[10]:= errorExpr1 = Expand[MCPH] - Expand[Cp@avgT]

Out[11]=
C T1^2/12 - C T1 T2/6 + C T2^2/12
```

```
In[]:= errorExpr2 = Expand[ C/12 * (T1 - T2)^2 ]  
Out[]=  
C T1^2 - C T1 T2 + C T2^2  
12      6      12  
(*Use a "boolean" equation to see if the two expressions are equal*)  
errorExpr1 == errorExpr2 (  
Out[]=  
True
```

Comparison of expressions 1 and 2 shows they are equal. //ANS