Problem 4.22

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

Solution

Balanced Reaction:

C_5H_{12} (g) + 8 O_2 (g) → 5 CO_2 (g) + 6 H_2O (l)

```
(-393509) * 5 + (-285830) * 6 - (-146760) * 1 (*J/mol*)
```

−3535765

```
(*J per mole 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 deg F and 1 atm.

Solution

```
Quit[];
```

Balanced combustion reaction:

CH_4 (g) + 2 O_2 (g) → CO_2 (g) + 2 H_2O (liq)

```
HHV = (-393509) * 1 + (-285830) * 2 - (-74520) * 1 (*J per mol CH4*)
```

-890 649

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

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

```
T = (60 + 459.67) * degR;
```

$$v = \frac{150\,000\,000 * \frac{ft^3}{d} * 1\ atm}{R * T} * \frac{1000\ gmol}{2.20462\ lbmol}$$

$$\frac{1.79303200362 \times 10^8\ gmol}{d}$$

$$\frac{1.79303 * 10^8\ gmol}{d} * \frac{890\,649\ J}{gmol} * \frac{1\ GJ}{10^9\ J} * \frac{5\ dollars}{GJ}$$

$$\frac{798\,480.188235\ dollars}{d}$$

```
(*//ANS*)
```

Problem 4.71

Locate your name in the list below and use the DIPPR database to find the critical temperature and pressure for the compounds assigned to you. Report your results in tabular form in units of bar and K using the template in your

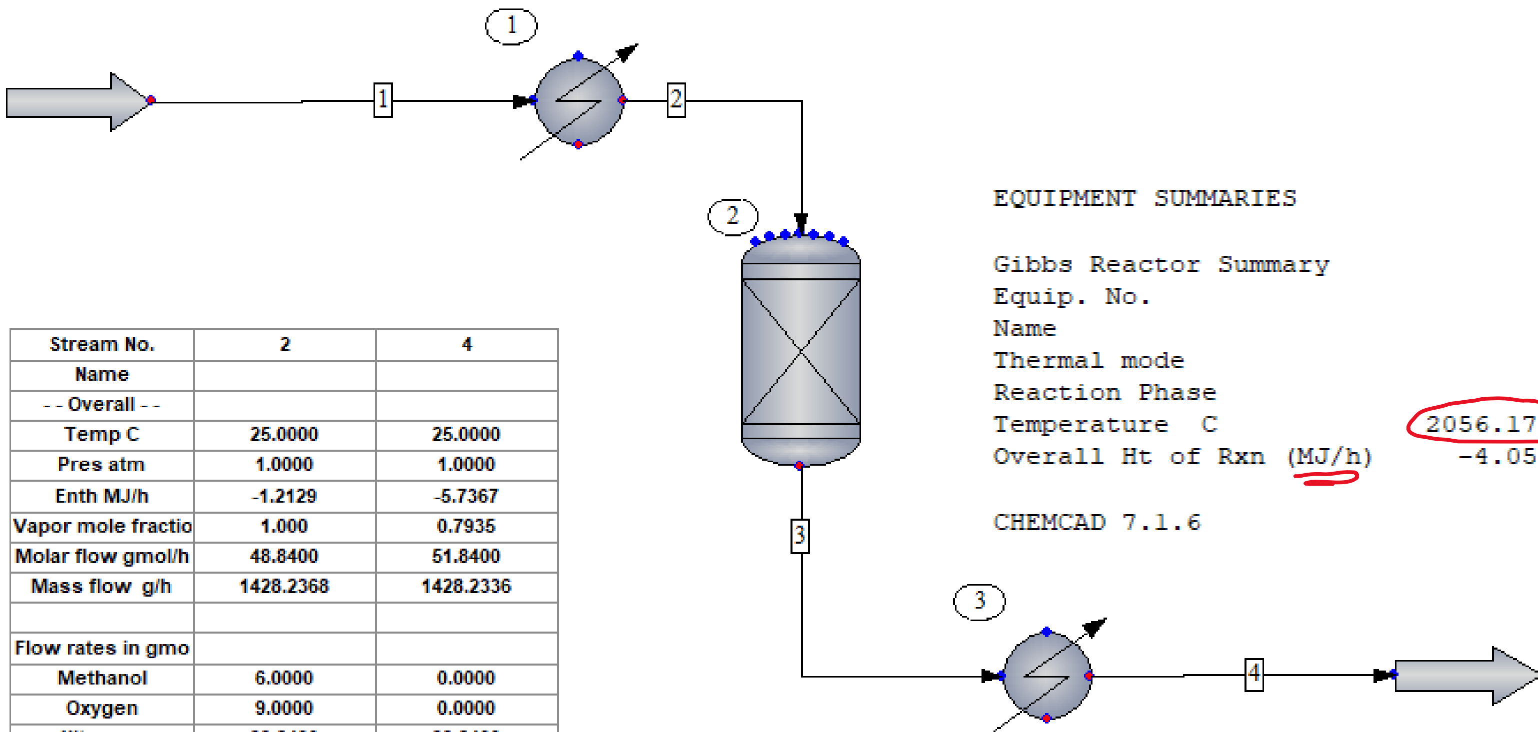
		T_c, K	P_c, bar		T_c, K	P_c, bar		T_c, K	P_c, bar
Baldwin	sodium chloride	3400	355.00	chlorine dioxide	465	86.1263	isoquinoline	803.15	51.00
Behr	bisphenol A	849	29.23	cyanogen chloride	449	59.9	acetoacetanilide	879	30.30
Benson	chlorine	417.75	77.10	chlorine trifluoride	433.7	45.78	p-cymene	652	28.00
Cianfaglione	piperazine	638	55.30	anisole	645.6	42.50	triethyl phosphate	757	68.40
Ibrahimi	pyridine	619.95	56.30	trans-2-hexene	509.8	31.68	naphthalene	748.4	40.50
Milanesa	acetone	508.1	47.00	sulfur dichloride	542	66.80	benzonitrile	702.3	42.15
Morrall	ethyl acetate	523.3	38.80	benzonitrile	702.3	42.15	camphor	709	29.90
Mossman	sodium hydroxide	2820	250.00	silicon dioxide	3780	31.60	cumene	631	32.09
Onaga	ethanol	514	61.37	anethole	723	29.00	dibenzyl ether	777	25.60
Weathers	fluorine	144.12	51.724	triethylene glycol	769.5	33.20	cetyl methacrylate	793	12.30
Weaver	benzene	562.05	48.95	trans-3-hexene	509	31.70	cetane	722	13.73
Bennett, S	cis-3-hexene	509	31.70	acetaldoxime	568	60.40	phosgene	455	56.742
Cesarski	methyl methacrylat	566	36.80	2-chloroethanol	585	59.20	diethyl sulfide	557.15	39.60
Dolin	allyl alcohol	545.1	56.2	diethanolamine	736.6	42.70	ammonium sulfide	479	31.54
Goulet	iodine	819.15	116.54	crotyl glycol ether	643.9	33.87	methyl mercaptan	469.95	72.30
Johnson	quinoline	782.15	48.60	2-mercaptoethanol	629	62.70	pyrazine	626	54.90
Kotkin	acridine	905	36.40	ethylthioethanol	641	43.20	pyrazole	734	66.00
Murray	1,3 dioxane	590	51.50	2-butanol	535.9	41.885	carbon monoxide	132.92	34.99
Patel	niacin	760	46.40	thiodiglycol	731	46.10	isoxazole	590	61.00
Sullivan	acrylonitrile	540	46.60	triethanolamine	772.1	27.43	caprolactam	818.2	46.21
Williams	n-tricosane	800.3	92.90	allyl methacrylate	600	30.20	graphite	6810	2230

Answer to Question:

DIPPR is the "Design Institute for Physical Properties," and was created by the AIChE in 1978 to cull thermodynamic

Problem 4.83

Hydrocarbon fuels such as methanol are used to store energy in liquid form. Flow calorimeters are frequently used to measure standard heats of reaction for liquid fuels. An example is shown in page 54. Use CHEMCAD to construct a simulation of a flow calorimeter that is designed to combust methanol in a stoichiometric amount of air. The feed mixture enters the process at 20 deg C and must be preheated to 25 deg C before entering the reactor. The reactor effluent must be cooled to 25 deg C before discharge to the atmosphere. Compare the heat of reaction from CHEMCAD to the value obtained in Problem 4.20.




```
EQUIPMENT SUMMARIES

Gibbs Reactor Summary
Equip. No.                          2
Name
Thermal mode                        1
Reaction Phase                      1
Temperature  C              2056.1731
Overall Ht of Rxn (MJ/h)      -4.0573

CHEMCAD 7.1.6
```

Stream No.	2	4
Name		
- - Overall - -		
Temp C	25.0000	25.0000
Pres atm	1.0000	1.0000
Enth MJ/h	-1.2129	-5.7367
Vapor mole fractio	1.000	0.7935
Molar flow gmol/h	48.8400	51.8400
Mass flow g/h	1428.2368	1428.2336
Flow rates in gmo		
Methanol	6.0000	0.0000
Oxygen	9.0000	0.0000
Nitrogen	33.8400	33.8400
Carbon Dioxide	0.0000	6.0000
Water	0.0000	12.0000

The CHEMCAD Gibbs Reactor gives a calculated value of -4.0573 MJ per hour. Since the flow rates are specified in mol per hour, this is equivalent to -4.0573 MJ per 6 moles of CH3OH. This is very close to the value of 4.0589 MJ per 6 moles of CH3OH obtained in Problem 4.20. The difference is probably due to slight differences in the standard state gas phase heats of formation in the CHEMCAD database. We also note here that the heat duty on exchanger 3 is -4.5238 MJ. This accounts for the sensible heat contributions from Nitrogen, which are not included in the calculation of the standard heat of reaction.

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?

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:

$$C_4H_8\ (g) + 10 H_2O\ (g) \rightarrow C_4H_6\ (g) + H_2\ (g) + 10\ H_2O\ (g)$$

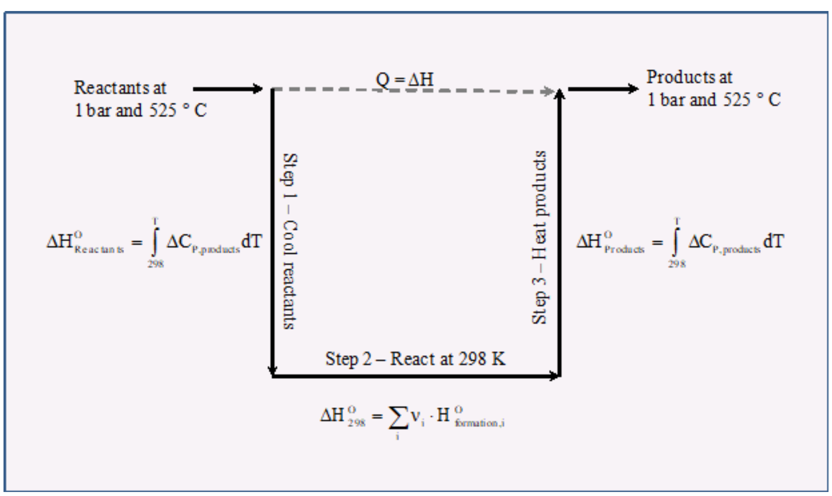
In[∘]:=
```
(*Stoichiometric coefficients*)
(*1-butene, water, 1,3-butadiene, hydrogen, water*)
ν = {-1, -10, 1, 1, 10};
```

In[∘]:=
```
(*Standard Heats of Formation*)
(*1-butene,1,3-butadiene,hydrogen*)
ΔHf298 = {-540, -241 818, 109 240, 0.000, -241 818};
```

In[∘]:=
```
(*Heat of Reaction at 298 K*)
ΔH298 = Plus @@ ν (* ΔHf298 ) (*J/mol*)
```

Out[∘]=
```
109 780.
```

Assume that the reactants enter the process at 525 deg 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 deg C because the standard heat of reaction is known at 25 deg C. In step 2, the reaction occurs at 25 deg C. In step 3, the products are heated back up to 525 deg 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. However, we will include it in this solution. If the reactants entered at a different temperature than the products, water would definitely need to be included in the enthalpy integrals.



```
(*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, 0.121, 0.000, 0.083, 0.121} * 10^5;

(*Stoichiometric coefficients*)
(*1-butene, water, 1,3-butadiene, hydrogen, water*)
(*same as before - re-defined only if feed is at T0*)
ν = {-1, -10, 1, 1, 10};
```

In[∘]:=
```
Δa = Plus @@ (ν * a);
Δb = Plus @@ (ν * b);
Δc = Plus @@ (ν * c);
Δd = Plus @@ (ν * d);
```

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

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

```
(*Equation 4.21 for MCPH*)
```

$$MCPH = \Delta a + \frac{\Delta b}{2} * (T + T0) + \frac{\Delta c}{3} * (T^2 + T0^2 + T * T0) + \frac{\Delta d}{T * T0};$$

```
(*Equation 4.22 for corrected heat of
reaction*) (*Gives molar heat of reaction in J/
mol*) ΔH798 = ΔH298 + MCPH * R * (T - T0)
```

Out[∘]= 117 867.

```
(*Heat requirement in J per mole of C4H8*)
Q = .33 * ΔH798
```

Out[∘]= 38 896.1

```
(*//ANS*)
```

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 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?

Solution to 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:
$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O$
$C_2H_6 + \frac{7}{2}\ O_2 \rightarrow 2\ CO_2 + 3\ H_2O$

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

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

        (*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 @@ ν (* ΔHf298 ) (*-825.09645 kJ per mole of natural gas feed //ANS*)

Out[•]= -825096.45
```

Solution to Part (b)

There is no heat requirement to warm or cool the reactants so we consider only the products in the application of Equation 4.20. This means the list of coefficients is changed to reflect just the products.

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

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

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

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

In[•]:= (*Equation 4.21 for MDCPH*)
        MDCPH = Δa + Δb/2 * (T1 + T0) + Δc/3 * (T1^2 + T0^2 + T1 * T0) + Δd/(T1 * T0)

Out[•]= 60.9018581

        (*Use Equation 4.21 for corrected heat of reaction in J/mol*)
        ΔH873 = ΔH298 + MDCPH * R * (T1 - T0)

Out[•]= -533952.0722

        (*Calculated units are J/mol of natural gas feed *)
        (*Q=ΔH873=-533,952 J/mol = -533.952 kJ/mol //ans*)
```

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 $\langle C_P \rangle_H$ 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[ ]:=
```
Quit[];
```

In[ ]:=
```
Cp[T_] = A + B * T + C * T^2;
(*Cp evaluated at the arithmetic mean temperature*)
Cp@avgT = Cp[(T1 + T2)/2]
```

Out[ ]=

$$A + \frac{1}{2} B\ (T1 + T2) + \frac{1}{4} C\ (T1 + T2)^2$$

```
(*MCPH which is equal to ⟨Cp⟩H*)
MCPH = A + B/2 (T2 + T1) + C/3 * (T2^2 + T1^2 + T2 * T1)
```

Out[ ]=

$$A + \frac{1}{2} B\ (T1 + T2) + \frac{1}{3} C\ \left(T1^2 + T1\ T2 + T2^2\right)$$

```
(*Demonstration of the Expand function to see what it does.*)
Expand[Cp@avgT]
```

In[ ]:=

$$A + \frac{B\ T1}{2} + \frac{C\ T1^2}{4} + \frac{B\ T2}{2} + \frac{C\ T1\ T2}{2} + \frac{C\ T2^2}{4}$$

Out[ ]=

$$A + \frac{B\ T1}{2} + \frac{C\ T1^2}{4} + \frac{B\ T2}{2} + \frac{C\ T1\ T2}{2} + \frac{C\ T2^2}{4}$$

In[ ]:=
```
Expand[MCPH]
```

Out[ ]=

$$A + \frac{B\ T1}{2} + \frac{C\ T1^2}{3} + \frac{B\ T2}{2} + \frac{C\ T1\ T2}{3} + \frac{C\ T2^2}{3}$$

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

In[ ]:=
```
expr1 = Expand[MCPH] - Expand[Cp@avgT]
```

Out[ ]=

$$\frac{C\ T1^2}{12} - \frac{C\ T1\ T2}{6} + \frac{C\ T2^2}{12}$$

In[ ]:=
```
expr2 = Expand[C/12 * (T1 - T2)^2]
```

Out[ ]=

$$\frac{C\ T1^2}{12} - \frac{C\ T1\ T2}{6} + \frac{C\ T2^2}{12}$$

```
expr1 == expr2
 (*question - does expr1=expr2? - a "boolean" equation - answer is true or false*)
```

Out[ ]=

```
True
```

Comparison of expressions 1 and 2 shows they are equal.