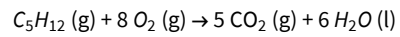


Problem 4.22

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:



$$(-393\,509) * 5 + (-285\,830) * 6 - (-146\,760) * 1 \text{ (*J/mol*)}$$

$$-3\,535\,765$$

(*J per mole n-pentane*)

(* //ANS*)

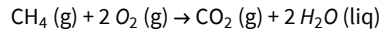
Problem 4.28

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:



$$\text{HHV} = (-393\,509) * 1 + (-285\,830) * 2 - (-74\,520) * 1 \quad (*\text{J per mol CH}_4*)$$

$$-890\,649$$

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

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

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

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

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

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

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

(*//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

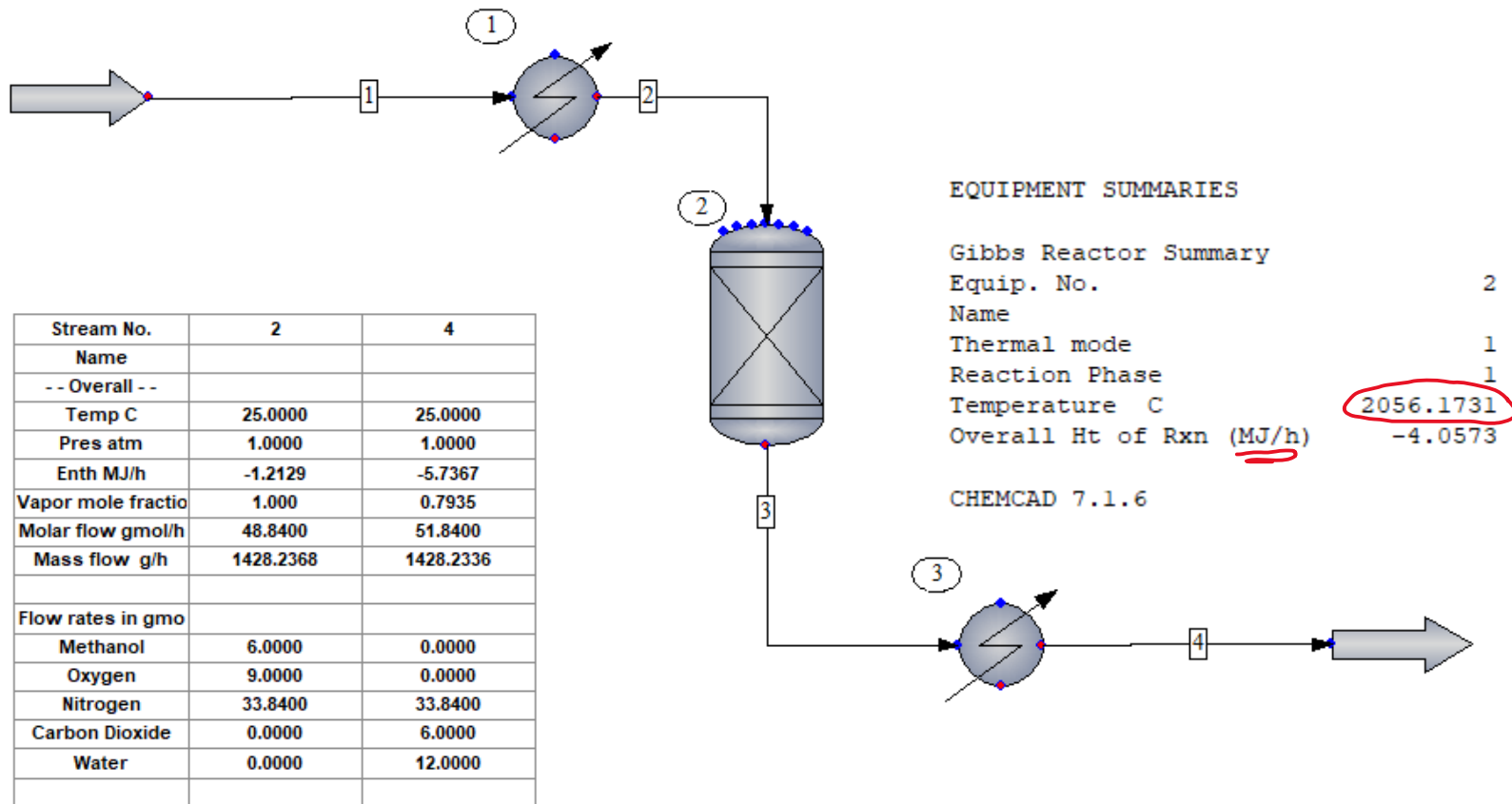
		T_c , K	P_c , bar		T_c , K	P_c , bar		T_c , K	P_c , bar
Dawson	sodium chloride	3400	355	chlorine dioxide	465	86.1263	isoquinoline	803.15	51.00
Harrison	bisphenol	849	29.23	cyanogen chloride	449	59.9	acetoacetanilide	879	30.30
Kim	sodium chloride	3400	355	chlorine dioxide	465	86.1263	isoquinoline	803.15	51.00
Lucero	chlorine	417.15	77.10	chlorine trifluoride	433.7	45.78	p-cymene	652	28.00
Romsland	piperazine	638	55.30	anisole	645.6	42.50	triethyl phosphate	757	68.40
Tuttle	pyridine	619.95	56.30	trans-2-hexene	509.8	31.68	naphthalene	748.4	40.50
Bedor	cis-2-hexene	511.4	31.60	methyl iodide	528.2	66.00	n-undecane	639	19.50
Bomke	cis-3-hexene	509	31.70	acetaldoxime	568	60.40	phosgene	455	56.742
Hawang	methyl methacrylat	566	36.80	2-chloroethanol	585	59.20	diethyl sulfide	557.15	39.60
Komorowski	allyl alcohol	545.1	56.2	diethanolamine	736.6	42.70	ammonium sulfide	479	31.54
Liesen	iodine	819.15	116.54	crotyl glycol ether	643.9	33.87	methyl mercaptan	469.95	72.30
Sawyer	quinoline	782.15	57.76	2-mercaptoethanol	629	62.70	pyrazine	626	54.90
Taptich	acridine	905	29.70	ethylthioethanol	641	43.20	pyrazole	734	66.00
Zlotnick	niacin	760	46.40	thiodiglycol	731	46.10	isoxazole	590	61.00

Answer to Question:

DIPPR is the "Design Institute for Physical Properties," and was created by the AIChE in 1978 to cull thermodynamic data from worldwide citations and to provide a single database for the data.

Problem 4.83

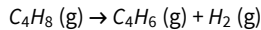
Hydrocarbon fuels such as methanol are used to store energy in liquid form. Flow calorimeters are frequently used to measure standard heats of reaction for liquid fuels. An example is shown in page 54. Use CHEMCAD to construct a simulation of a flow calorimeter that is designed to combust methanol in 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.



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

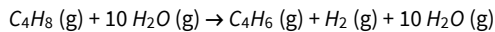
A process for the production of 1,3-butadiene results from the catalytic dehydrogenation at atmospheric pressure of 1-butene according to the reaction:



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:



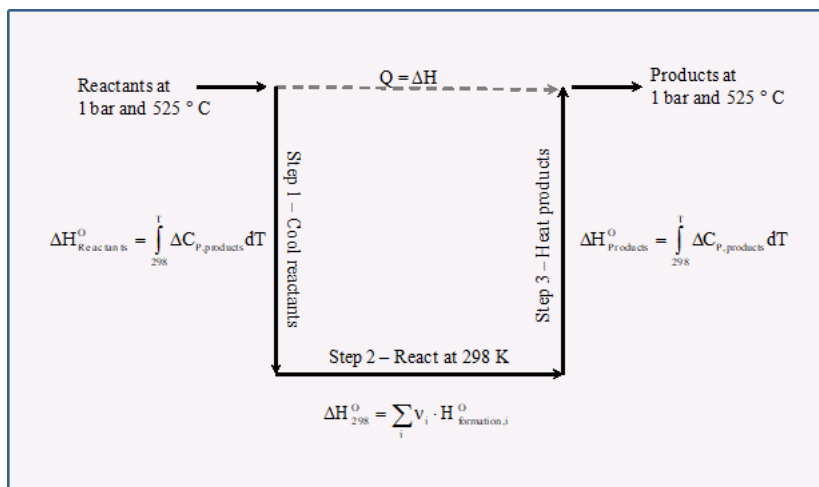
$ln[] :=$ (*Stoichiometric coefficients*)
 (*1-butene, water, 1,3-butadiene, hydrogen, water*)
 $v = \{-1, -10, 1, 1, 10\};$

$ln[] :=$ (*Standard Heats of Formation*)
 (*1-butene, 1,3-butadiene, hydrogen*)
 $\Delta H_f^{298} = \{-540, -241818, 109240, 0.000, -241818\};$

$ln[] :=$ (*Heat of Reaction at 298 K*)
 $\Delta H_{298} = \text{Plus @@ } (v * \Delta H_f^{298}) \text{ (*J/mol*)}$

$Out[] :=$ 109780.

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. The “short” solution in this solution packet is worked without water.



```

(*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} * 105;

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

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

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

(*Equation 4.21 for MCPH*)

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


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

Out[ ]:= 117867.

(*Heat requirement in J*)
Q = .33 * ΔH798

Out[ ]:= 38896.1

(* //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?

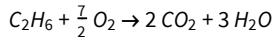
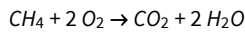
Solution to Part (a)

Balanced Chemical Equations, assuming carbon dioxide and water as products

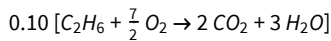
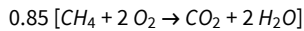
All species are gas-phase.

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

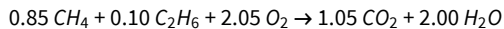
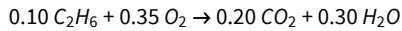
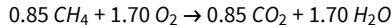
Step 1 - Balance the reactions:



Step 2 - Multiply the reactions by the feed composition:



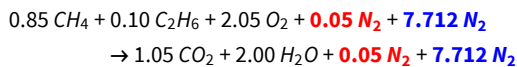
Step 3 - Add the reactions:



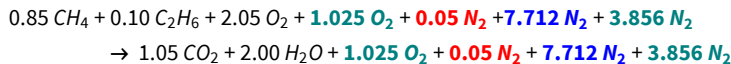
Step 4 - Add the **0.05 N_2** that comes in with the natural gas::



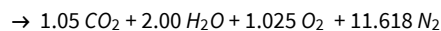
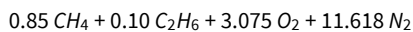
Step 5 - Add the nitrogen that enters with the air ($2.05 \times 79/21 = \mathbf{7.712 N_2}$):



Step 6 - Add the excess air ($2.05 \times 0.5 = \mathbf{1.025 O_2}$ and $7.712 \times 0.5 = \mathbf{3.856 N_2}$):



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



```

In[*]:= (*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};

(*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 ) (*-825.09645 kJ per mole of 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*)
v = {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} * 105;

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

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

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

In[*]:= (*Equation 4.21 for MDCPH*)
MDCPH = Δa +  $\frac{\Delta b}{2} * (T1 + T0) + \frac{\Delta c}{3} * (T1^2 + T0^2 + T1 * T0) + \frac{\Delta d}{T1 * T0}$ 

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 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*)

$$Cp@avgT = Cp\left[\frac{T_1 + T_2}{2}\right]$$

Out[]:=

$$A + \frac{1}{2} B (T_1 + T_2) + \frac{1}{4} C (T_1 + T_2)^2$$

(*MCPH which is equal to $\langle C_p \rangle_H$ *)

$$MCPH = A + \frac{B}{2} (T_2 + T_1) + \frac{C}{3} * (T_2^2 + T_1^2 + T_2 * T_1)$$

Out[]:=

$$A + \frac{1}{2} B (T_1 + T_2) + \frac{1}{3} C (T_1^2 + T_1 T_2 + T_2^2)$$

(*Demonstration of the Expand function to see what it does.*)

Expand[Cp@avgT]

$$In[]:= A + \frac{B T_1}{2} + \frac{C T_1^2}{4} + \frac{B T_2}{2} + \frac{C T_1 T_2}{2} + \frac{C T_2^2}{4}$$

Out[]:=

$$A + \frac{B T_1}{2} + \frac{C T_1^2}{4} + \frac{B T_2}{2} + \frac{C T_1 T_2}{2} + \frac{C T_2^2}{4}$$

In[]:= **Expand[MCPH]**

Out[]:=

$$A + \frac{B T_1}{2} + \frac{C T_1^2}{3} + \frac{B T_2}{2} + \frac{C T_1 T_2}{3} + \frac{C T_2^2}{3}$$

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

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

Out[]:=

$$\frac{C T_1^2}{12} - \frac{C T_1 T_2}{6} + \frac{C T_2^2}{12}$$

```
In[ ]:= expr2 = Expand $\left[\frac{C}{12} * (T1 - T2)^2\right]$ 
```

```
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.