

Problem 4.5

How much heat is required when 10,000 kg of CaCO_3 is heated at atmospheric pressure from 50 deg C to 880 deg C? Use (a) direct integration of the C_p polynomial, (b) ICPH, and (c) MCPH.

Solution

Method 1 - Integrate the Heat Capacity Polynomial Directly

The question is answered with three different methods. The most apparent is direct integration of the heat capacity polynomial, Eq. 4.5. The constants for the heat capacity polynomial are found in Table C.2 on page 657.

```
In[ ]:= Quit[ ];

In[ ]:= a = 12.572; (*Table C.2*)
b = 2.637 * 10-3;
c = 0;
d = -3.12 * 105;

In[ ]:= Cp[T_] = a + b * T + d * T-2;

In[ ]:= T0 = 50 + 273.15; (*K*)
T1 = 880 + 273.15;
R = 8.314; (*  $\frac{\text{J}}{\text{mol} \cdot \text{K}}$  *)

In[ ]:= Q = R *  $\int_{T0}^{T1} \text{Cp}[x] \, dx$  (*Units come from R - J/mol*)

Out[ ]:=
94408.9920314

In[ ]:= Q *  $\frac{\text{J}}{\text{mol}}$  *  $\frac{1 \text{ mol}}{100.087 \text{ g}}$  * 10000 kg *  $\frac{1000 \text{ g}}{\text{kg}}$  *  $\frac{1 \text{ MJ}}{10^6 \text{ J}}$  (*ANS*)

Out[ ]:=
9432.69276044 MJ
```

The next two methods illustrate the use of the integrated forms of the heat capacity, namely ICPH and MCPH.

Method 2 - ICPH, Eq 4.8

```
In[ ]:= ICPH = a * (T1 - T0) +  $\frac{b}{2} * (T1^2 - T0^2) + \frac{c}{3} * (T1^3 - T0^3) + d * \left( \frac{T1 - T0}{T1 * T0} \right)$ 

Out[ ]:=
11355.4236266

In[ ]:= Q = R * ICPH

Out[ ]:=
94408.9920314
```

$$\text{In[]:= } Q * \frac{\text{J}}{\text{mol}} * \frac{1 \text{ mol}}{100.087 \text{ g}} * 10000 \text{ kg} * \frac{1000 \text{ g}}{\text{kg}} * \frac{1 \text{ MJ}}{10^6 \text{ J}} (*\text{ANS}*)$$

Out[]:=

9432.69276044 MJ

Method 3 - MCPH, Eq 4.9

$$\text{In[]:= } \text{MCPH} = a + \frac{b}{2} * (T1 + T0) + \frac{c}{3} (T1^2 + T0^2 + T1 * T0) + \frac{d}{T1 * T0}$$

Out[]:=

13.681233285

$$\text{In[]:= } Q = R * \text{MCPH} * (T1 - T0)$$

Out[]:=

94408.9920314

$$\text{In[]:= } Q * \frac{\text{J}}{\text{mol}} * \frac{1 \text{ mol}}{100.087 \text{ g}} * 10000 \text{ kg} * \frac{1000 \text{ g}}{\text{kg}} * \frac{1 \text{ MJ}}{10^6 \text{ J}} (*\text{ANS}*)$$

Out[]:=

9432.69276044 MJ

Problem 4.9

A process stream is heated as a gas from 25 to 250 deg C at constant P. A quick estimate of the energy requirement is obtained from Eq. 4.3, with Cp taken as constant and equal to its value at 25 deg C. Is the estimate of Q likely to be low or high? Why?

Solution

This question is best answered with a calculation. While the fluid identity is unspecified, we can use a representative ideal gas, such as nitrogen. Nitrogen appears in the plot in Figure 4.1 in the textbook showing heat capacity as a function of temperature, but not the temperature range given in this problem. Use Table C.1 on page 656 along with Eq. 4.3 to construct and integrate the heat capacity polynomial.

It is important to point out that the sample calculation shown here does not represent a general solution to this answer, but is only illustrative.

Quit [] ;

```
In[ ]:= a = 3.280; (*Table C.1*)  
b = 0.593 / 1000;  
d = 0.040 / 10-5;
```

```
In[ ]:= Cp[T_] = a + b * T + d * T-2;  
  
T1 = 25 + 273.15; (*K*)  
T2 = 250 + 273.15;  
R = 8.314; (*  $\frac{\text{J}}{\text{mol}\cdot\text{K}}$  *)
```

```
In[ ]:= Q = R *  $\int_{T1}^{T2}$  Cp[x] dx (*J/mol*)
```

```
Out[ ]:=  
6639.23658097
```

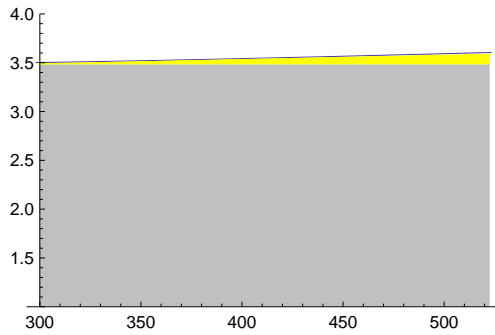
Cp298 = 3.502; (*Table 3.1*)

```
In[ ]:= R * Cp298 * (250 - 25)
```

```
Out[ ]:=  
6551.0163
```

As can be seen in these two results, the heat estimate from the constant Cp is low. The estimate is low in this case because the heat capacity, which is a function of the temperature, increases with temperature. This can be seen in Figure 4.1 in the textbook. Using a constant heat capacity taken from the left side of the plot will underestimate the value of the area under the curve. Since the heat is equal to the integral of the curve, underestimating the area under the curve will underestimate the heat. This is illustrated in the plot below. The gray shaded area represents the integral of the heat capacity assuming a constant Cp. The yellow triangle represents the difference in the integrated areas.

Plot[Cp[T], {T, T1, T2}, PlotRange -> {1, 4}]



The reason that the heat capacity increases with temperature is that additional vibrational and rotational modes are available to the molecules to store heat energy. Note that this does not happen with molecules like Argon (see Fig. 4.1). This is because the molecule is monatomic and spherical in shape and does not vibrate or rotate the same way that the polyatomics do. You can see this if you think about the chemical bond as a spring with two masses attached to the ends from classical mechanics. The spring stretches and compresses in a manner similar to the chemical bond. These stretches and compressions act as a reservoir for thermal energy.

Problem 4.10

(a) For one of the compounds listed in Table B.2 of App. B, evaluate the latent heat of vaporization ΔH_n by Eq. 4.13. How does this result compare with the value listed in Table B.2?

(b) Handbook values for latent heats of vaporization at 25 deg C of four compounds are given in the table below. Calculate ΔH_n by Eq. 4.14, and compare the result with the value given in Table B.2.

Latent heats of vaporization at 25 deg C in J/g			
n-Pentane	366.3	Benzene	433.3
n-Hexane	366.1	Cyclohexane	392.5

Solution

Part (a) - Latent Heats by Eq. 4.13 (Riedel Equation)

```
Quit[];

(*n-Pentane*)
Tn = 309.2; (*K, Table B.1 page 663*)
Tc = 469.7; (*K, Table B.1 page 663*)
Trn = Tn / Tc;
Pc = 33.70; (*bar*)
R = 8.314; (*  $\frac{\text{J}}{\text{mol}\cdot\text{K}}$  *)

$$\Delta H_n = R * T_n * \frac{1.092 * (\text{Log}[Pc] - 1.013)}{0.930 - Trn} \quad (*\text{J/mol}*)$$

```

Out[]:=

25 875.6472317

(*The value given in Table B.2 is 25.79 kJ/mol which shows 0.33% error*)

$$\frac{25.876 - 25.79}{25.79} * 100$$

(*ANS*)

Out[]:=

0.333462582396

Part (b) - Latent heats by Eq. 4.14

This solution used *Mathematica* “lists” to answer the question for all four compounds simultaneously. In the work that follows, the list order is {n-Pentane, n-Hexane, Benzene, Cyclohexane}.

```
In[ ]:= Quit[];

(*ΔH1 in J/g at 25 deg C is given in the problem above*)
ΔH1 = {366.3, 366.1, 433.3, 392.5}; (*J/g*)
T1 = 298.15; (*K given in problem statement*)
(*Tn (which is T2) and Tc in K are look-ups in App B pp. 663-665*)
T2 = {309.2, 341.9, 353.2, 353.9};
Tc = {469.7, 507.6, 562.2, 553.6}; (*K, look up*)
Tr2 = T2 / Tc;
Tr1 = T1 / Tc;
```

```
In[ ]:= 
$$\Delta H2 = \Delta H1 * \left( \frac{1 - Tr2}{1 - Tr1} \right)^{0.38} (*J/g*)$$

```

```
Out[ ]:= {357.148604984, 334.91279798, 396.463793804, 357.443234241}
```

```
(*MW is in App B pp. 663-665*)
```

```
MW = {72.150, 86.177, 78.114, 84.160};
```

```

$$\Delta H2_{pm} = \Delta H2 * MW / 1000 (*kJ/mol*)$$

```

```
Out[ ]:= {25.7682718496, 28.8617801915, 30.9693727892, 30.0824225938}
```

```
In[ ]:= (*The values of  $\Delta H_n$  are given in Table B.2 in kJ/mol as:*)
```

```

$$\Delta H_n = \{25.79, 28.85, 30.72, 29.97\};$$

```

```
In[ ]:= (*Answers are compared by percent errors*)
```

```

$$\frac{\Delta H_n - \Delta H2_{pm}}{\Delta H_n} * 100 (*ANS*)$$

```

```
Out[ ]:= {0.0842502924755, -0.0408325527918, -0.811760381599, -0.375117096279}
```

Problem 4.12

Handbook values for the latent heat of vaporization in J/g are given in the table for several pure liquids at 0 deg C.

	ΔH at 0 deg C
Chloroform	270.9
Methanol	1,189.5
Tetrachloromethane	217.8

Calculate:

- (a) The value of the latent heat at T_n by Eq. 4.14, given the value at 0 deg C.
- (b) The value of the latent heat at T_n by Eq. 4.13.

By what percentage do these results differ from the value listed in Table B.2 of App. B?

Solution

Part (a) - Latent heats by Eq. 4.14

Cadets are required to do this calculation for three substances. This solution in Parts (a) and (b) use *Mathematica* "lists" to answer all three compounds simultaneously. The list order is {chloroform, methanol, tetrachloromethane}.

Quit[];

$\Delta H1 = \{270.9, 1189.5, 217.8\}; (*J/g, given*)$

$T1 = 273.15; (*K, given*)$

$T2 = \{334.3, 337.9, 349.8\}; (*Tn \text{ in } K*)$

$Tc = \{536.4, 512.6, 556.4\}; (*K*)$

$Tr2 = T2 / Tc;$

$Tr1 = T1 / Tc;$

$\Delta H2 = \Delta H1 * \left(\frac{1 - Tr2}{1 - Tr1} \right)^{0.38} (*J/g*)$

{245.010231031, 1055.19836726, 193.189192365}

$MW = \{119.377, 32.042, 153.822\};$

$\Delta H2pm = \Delta H2 * MW / 1000 (*kJ/mol*)$

{29.2485863497, 33.8106660838, 29.716747948}

(*The values of ΔHn are given in Table B.2 in kJ/mol as:*)

$\Delta Hn = \{29.24, 35.21, 29.82\};$

(*Percent error*)

$\frac{\Delta Hn - \Delta H2pm}{\Delta Hn} * 100 (*//ANS*)$

{-0.0293650811832, 3.97425139501, 0.346251012815}

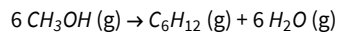
Part (b) - Latent heats by Eq. 4.13

```
(*Pc is in App B pp. 663-665*)
Pc = {54.72, 80.97, 45.60}; (*bar*)
R = 8.314; (*  $\frac{\text{J}}{\text{mol}\cdot\text{K}}$  from App A.*)
ΔH2 = R * T2 *  $\frac{1.092 * (\text{Log}[Pc] - 1.013)}{0.930 - \text{Tr2}}$  *  $\frac{1}{1000}$  (*kJ/mol*)
{29.5742585793, 38.3008975024, 29.5841421618}

(*Percent error*)
 $\frac{\Delta H_n - \Delta H_2}{\Delta H_n} * 100$  (*//ANS*)
{-1.14315519605, -8.77846493146, 0.790938424702}
```


Problem 4.20

Hydrocarbon fuels can be produced from methanol by reactions such as the following, which yields 1-hexene:

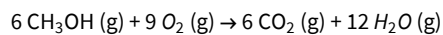


Compare the standard heat of combustion at 25 deg C of 6 $\text{CH}_3\text{OH} (\text{g})$ with the standard heat of combustion at 25 deg C of $\text{C}_6\text{H}_{12} (\text{g})$ for reaction products $\text{CO}_2 (\text{g})$ and $\text{H}_2\text{O} (\text{g})$.

Solution

Quit [] ;

6 Methanols

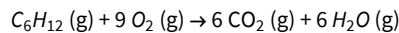


(*Table C.4 values: CO2: -393509 H2O(g): -241818 CH3OH(g): -200660*)

(-393509) * 6 + (-241818) * 12 - (-200660) * 6 (*//ANS J/mol*)

-4058910

1-Hexene



(*Table C.4 values: C6H12(g): -41950*)

(-393509) * 6 + (-241818) * 6 - (-41950) * 1 (*//ANS pJ/mol*)

-3770012

The heat of combustion of methanol is a somewhat higher than 1-hexene, which raises the question of whether or not to actually invest in the process to do the conversion. In making this decision, there would be tradeoffs between economic factors such as the value of the amount of energy stored in the fuel and other factors such as pollution and emissions, process hazards and safety, and corrosion. Each of these factors would need to be given weight in the cost-benefit analysis. (ANS)

Lesson 17 Bonus:

Submission needs (1) CHEMCAD work, (2) completed table from Lesson 17 slide 13, and (3) explanation of the difference between CHEMCAD's heat duty and the heat of reaction in the Gibbs isothermal reactor. CHEMCAD work is +1 and the explanation is +4.