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## Problem Set 6 - Solutions

### Problem 4.5

How much heat is required when 10,000 kg of  $\text{CaCO}_3$  is heated at atmospheric pressure from 50 to 880 °C? Use (a) direct integration of the  $C_p$  polynomial, (b) ICPH, and (c) MCPH. Report your answers in MJ.

#### (a) Direct Integration of the $C_p$ Polynomial

```
In[*]:= a = 12.572; (*Table C.2 page 670*)
```

```
b = 2.637 * 10-3;
```

```
c = 0;
```

```
d = -3.12 * 105;
```

```
In[*]:= Cp = a + b * T + d * T-2; (*Equation 4.5*)
```

```
In[*]:= T0 = 50 + 273.15; (*K*)
```

```
T1 = 880 + 273.15;
```

```
R = 8.314; (* $\frac{\text{J}}{\text{mol}\cdot\text{K}}$ *)
```

```
In[*]:= Q = R *  $\int_{T0}^{T1} C_p dT$  (*Units come from R - J/mol*)
```

```
Out[*]=
```

```
94408.99
```

```
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[*]=
```

```
9432.693 MJ
```

9432.69 MJ of heat energy is required. //ANS

#### (b) 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[*]=
```

```
11355.42
```

```
In[*]:= Q = R * ICPH
```

```
Out[*]=
```

```
94408.99
```

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

Out[\*]=

9432.693 MJ

9432.69 MJ, same as part (a). //ANS

(c) 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[\*]=

13.68123

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

Out[\*]=

94408.99

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

Out[\*]=

9432.693 MJ

9432.69 MJ, same as part (a). //ANS

## Problem 4.9

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

## Solution

This question is 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, so we will re-build this plot. Use Table C.1 on page 656 along with Eq. 4.3 to construct, plot, 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.

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

In[*]:= Cp = a + b * T + d * T-2; (*Equation 4.5*)

In[*]:= T1 = 25 + 273.15; (*K*)
T2 = 250 + 273.15;
R = 8.314; (*  $\frac{\text{J}}{\text{mol}\cdot\text{K}}$  *)

In[*]:= Q = R *  $\int_{T1}^{T2} Cp \, dT$  (*  $\frac{\text{J}}{\text{mol}}$  *)

Out[*]=
6639.237

In[*]:= Cp298 = 3.502; (*Table 3.1 in  $\frac{\text{J}}{\text{mol K}}$  *)

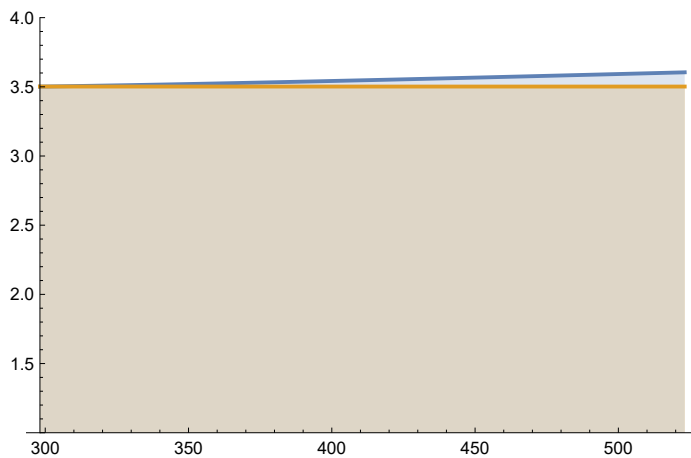
In[*]:= R * Cp298 * (250 - 25) (*  $\frac{\text{J}}{\text{mol}}$  *)

Out[*]=
6551.016
```

As can be seen in these two results, the heat estimate from the constant  $C_p$  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 bluish-amber shaded area represents the integral of the heat capacity assuming a constant  $C_p$ . The blue triangle represents the difference in the integrated areas.

```
In[ ]:= Plot[{Cp, Cp298}, {T, T1, T2}, PlotRange -> {1, 4}, Filling -> Bottom]
```

```
Out[ ]:=
```



The reason that the heat capacity increases with temperature is that as temperature is increased, 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 argon molecule is monatomic and spherical in shape and does not vibrate or rotate the same way that the polyatomic molecules do. You can see this if you think about the chemical bond as a spring with two masses attached to the ends described with classical mechanics. The spring can stretch and compress in a manner similar to the chemical bond. These stretches and compressions act as a reservoir for thermal energy.

## Problem 4.10

(a) Evaluate the latent heat of vaporization  $\Delta H_n$  of n-Pentane 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 °C of four compounds are given in the table below. Calculate  $\Delta H_n$  by Eq. 4.14, and compare the result with the value given in Table B.2.

Latent heats of vaporization at 25 °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 (Reidel Equation)

```
In[*]:= (*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; (*  $\frac{\text{J}}{\text{mol}\cdot\text{K}}$  *)

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

Out[*]=
25875.65

In[*]:= 
$$\frac{.001 \Delta H_n - 25.79}{25.79} * 100 \quad (*\text{percent error}*)$$

Out[*]=
0.3320947
```

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

### Solution - 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[*]:=  $\Delta H1 = \{366.3, 366.1, 433.3, 392.5\};$  (*Given in J/g at 25°C*)
T1 = 298.15; (*Given, K*)
T2 = {309.2, 341.9, 353.2, 353.9}; (*Tn in K from App B pp. 663-665*)
Tc = {469.7, 507.6, 562.2, 553.6}; (*T2 in K from App B pp. 663-665*)
Tr2 = T2 / Tc;
Tr1 = T1 / Tc;
```

```
In[*]:= ΔH2 = ΔH1 *  $\left(\frac{1 - Tr2}{1 - Tr1}\right)^{0.38}$  (*in J/g*)
```

```
Out[*]= {357.1486, 334.9128, 396.4638, 357.4432}
```

```
In[*]:= MW = {72.150, 86.177, 78.114, 84.160}; (*App B pp. 663-665*)
ΔH2pm = ΔH2 * MW / 1000 (*kJ/mol where "pm" is "per mol"*)
```

```
Out[*]= {25.76827, 28.86178, 30.96937, 30.08242}
```

```
In[*]:= ΔHn = {25.79, 28.85, 30.72, 29.97}; (*Table B.2 in kJ/mol.*)
```

```
In[*]:=  $\frac{\Delta Hn - \Delta H2pm}{\Delta Hn} * 100$  (*percent error*)
```

```
Out[*]= {0.08425029, -0.04083255, -0.8117604, -0.3751171}
```

The percent errors are shown above. //ANS

## 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 °C.

	$\Delta H$ at 0 °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 listed at 0 °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

The solutions in Parts (a) and (b) use *Mathematica* “lists” to answer all three compounds simultaneously. The list order is {chloroform, methanol, tetrachloromethane}.

```
In[*]:=  $\Delta H1 = \{270.9, 1189.5, 217.8\};$  (*in J/g, given*)
T1 = 273.15; (*K, given as 0°C*)
T2 = {334.3, 337.9, 349.8}; (*Tn in K from Table B.1*)
Tc = {536.4, 512.6, 556.4}; (*in K from Table B.1*)
Tr2 = T2 / Tc;
Tr1 = T1 / Tc;
```

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

```
Out[*]:= {245.0102, 1055.198, 193.1892}
```

```
In[*]:= MW = {119.377, 32.042, 153.822}; (*from Table B.1*)
 $\Delta H2pm = \Delta H2 * MW / 1000$  (*kJ/mol*)
```

```
Out[*]:= {29.24859, 33.81067, 29.71675}
```

```
In[*]:=  $\Delta Hn = \{29.24, 35.21, 29.82\};$  (* $\Delta Hn$  from Table B.2 in kJ/mol*)
```

```
In[*]:=  $\frac{\Delta Hn - \Delta H2pm}{\Delta Hn} * 100$  (*percent error*)
```

```
Out[*]:= {-0.02936508, 3.974251, 0.346251}
```

The percent errors are shown above. //ANS

## Solution - Part (b) - Latent Heats by Eq. 4.13

(\*Pc is in App B pp. 663-665\*)  
 $P_c = \{54.72, 80.97, 45.60\};$  (\*bar\*)  
 $R = 8.314;$  (\* $\frac{J}{mol \cdot K}$  from App A.\*)  

$$\Delta H_2 = R * T_2 * \frac{1.092 * (\text{Log}[P_c] - 1.013)}{0.930 - T_2} * \frac{1}{1000} \text{ (*kJ/mol*)}$$
 $\{29.57426, 38.3009, 29.58414\}$

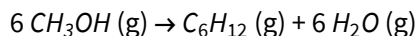
Comparison by percent error:

$$\frac{\Delta H_n - \Delta H_2}{\Delta H_n} * 100 \text{ (* // ANS*)}$$
 $\{-1.143155, -8.778465, 0.7909384\}$



## Problem 4.20

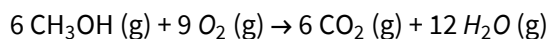
Hydrocarbon fuels can be produced from methanol by reactions such as the following, which yields 1-hexene:



Compare the standard heat of combustion at 25 °C of 6  $\text{CH}_3\text{OH} (\text{g})$  with the standard heat of combustion at 25 °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

### Six molecules of Methanol

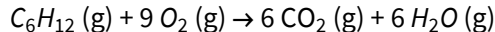


(\*Table C.4 values:  $\text{CO}_2$ : -393509  $\text{H}_2\text{O} (\text{g})$ : -241818  $\text{CH}_3\text{OH} (\text{g})$ : -200660\*)

```
In[*]:= ΔHm = (-393 509) * 6 + (-241 818) * 12 - (-200 660) * 6 (*//ANS, J/mol*)
```

```
Out[*]=
-4 058 910
```

### One molecule of 1-Hexene



(\*Table C.4 values:  $\text{C}_6\text{H}_{12} (\text{g})$ : -41950\*)

```
In[*]:= ΔHh = (-393 509) * 6 + (-241 818) * 6 - (-41 950) * 1 (*//ANS J/mol*)
```

```
Out[*]=
-3 770 012
```

```
In[*]:= ΔHm - ΔHh
```

```
Out[*]=
-288 898
```

The comparison is by difference, and we see that the combustion of 6  $\text{CH}_3\text{OH}$  releases more heat than one  $\text{C}_6\text{H}_{12}$  at standard conditions. The heat of combustion of  $\text{CH}_3\text{OH}$  is lower than that of  $\text{C}_6\text{H}_{12}$  by -288,898 J/mol. //ANS