Problem Set 2

Thermodynamics and Climate Change

MOSTEC 2021

1. **Concept questions:** Answer the following with a brief explanation.
   - (a) Under what conditions is the heat that is released in a chemical reaction given by (i) the change in enthalpy between products and reactants? and (ii) the change in internal energy?
   - (b) Is more heat released in a chemical reaction that occurs at constant volume or at constant pressure?
   - (c) Will the adiabatic flame temperature be higher or lower if air is used in combustion vs pure oxygen? (Both cases using stoichiometric quantities for ideal combustion).
   - (d) Why does burning pure elemental carbon (graphite) release heat despite it having no covalent bonds to break?
   - (e) (i) Coal is essentially sugar that has undergone pyrolysis. Would you expect coal or glucose to have a higher molar heating value? (ii) Which would you expect to have a higher carbon intensity?
   - (f) Why does a combustion reaction that produces liquid water release more heat than the same reaction that produces water vapor?

2. **Combustion Reactions:** For each of the following substances, write the balanced chemical equation for its ideal, stoichiometric combustion in air:
   - (a) Methanol (CH_3OH)
   - (b) Methane (CH_4)

Table 1: Enthalpies of formation for Problem 3

Species	Δh_f(1000°C) [MJ/kmol]
CO_2 (gas)	-393.5
CH_3OH (liquid)	-238.6
H_2O (vapor)	-241.8
H_2O (liquid)	-285.8

(c) Pentane (C_5H_{12})

(d) Coal (C)

(e) Magnesium (Mg)

3. **Forming of fuels:** Under the right conditions, including a high temperature (1000 °C) and pressure, pure carbon can react with liquid water to produce carbon dioxide and liquid methanol (CH_3OH). Though burning methanol still releases carbon dioxide, we are interested in determining whether using methanol as a fuel via this process produces as much greenhouse gas emissions for the same amount of heat compared to the original coal[1].

   (a) Write the chemical equation for this reaction.

   (b) What is the thermal energy required to produce 1 kmol of methanol? Enthalpies of formation for this process are given in Table 1.

   (c) What is the carbon intensity of burning pure coal in pure oxygen in units of kmol CO_2/MJ?

   (d) What is the carbon intensity of burning methanol produced in this process in pure oxygen in units of kmol CO_2/MJ? Assume water vapor is produced.

   (e) Does this process seem like a promising alternative to burning coal? Why or why not?

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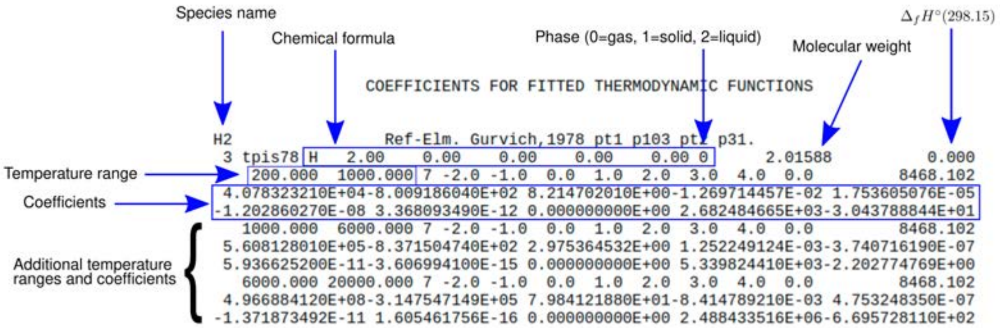
[1] This problem is adapted from 2.42, one of the graduate-level thermodynamics class taught at MIT.



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                    COEFFICIENTS FOR FITTED THERMODYNAMIC FUNCTIONS

H2                  Ref-Elm. Gurvich,1978 pt1 p103 pt2 p31.
 3 tpis78 H   2.00    0.00    0.00    0.00    0.00 0      2.01588        0.000
   200.000  1000.000 7 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0        8468.102
 4.078323210E+04-8.009186040E+02 8.214702010E+00-1.269714457E-02 1.753605076E-05
-1.202860270E-08 3.368093490E-12 0.000000000E+00 2.682484665E+03-3.043788844E+01
   1000.000  6000.000 7 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0        8468.102
 5.608128010E+05-8.371504740E+02 2.975364532E+00 1.252249124E-03-3.740716190E-07
 5.936625200E-11-3.606994100E-15 0.000000000E+00 5.339824410E+03-2.202774769E+00
   6000.000 20000.000 7 -2.0 -1.0  0.0  1.0  2.0  3.0  4.0  0.0        8468.102
 4.966884120E+08-3.147547149E+05 7.984121880E+01-8.414789210E-03 4.753248350E-07
-1.371873492E-11 1.605461756E-16 0.000000000E+00 2.488433516E+06-6.695728110E+02
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Figure 1: How to read NASA thermodynamic coefficients tables.

4. **Exploring Heat Capacity:** In this problem you will use Python code to explore the heat capacity of several substances. As we learned in class, heat capacity is a non-linear function with temperature and is determined empirically via experimentation. NASA has compiled the results of many such experiments to develop polynomial functions that accurately model the specific heat capacities of commonly used substances of the form

$$\frac{c_p(T)}{R} = a_1T^{-2} + a_2T^{-1} + a_3 + a_4T + a_5T^2 + a_6T^3 + a_7T^4 \tag{1}$$

where c_p is given in units of J/mol-K. Fig. 1 shows a sample coefficients table for hydrogen gas and what the various numbers mean. The coefficients in Eq. 1 are read from this table where it says "coefficients". Here a_1-a_7 are read from left to right, top to bottom. The first line contains a_1-a_5 and the second line contains a_6 and a_7 in the first two columns. See here for more information (page 43).

This information is provided here just to give you a sense for how these functions are modeled and implemented in code, but instead of having you rewrite these functions yourselves, I have gone ahead and done that for you in my simple nasaPoly library. For this problem and going forward, all coding assignments will be carried out in Google Colab. To begin, create a copy of the Problem Set 2 Colab Template. Using all of this information, answer the following questions using Python:

   (a) Plot c_p and c_v, each as functions of temperature for gaseous hydrogen, nitrogen, and carbon dioxide from 200-1000 K.

(b) Compare the thermal energy required to raise the temperature of each gas from 200-300 K at (i) constant pressure and (ii) constant volume. (iii) How do these answers differ when raising gas temperatures instead from 800-900 K? *Hint: You will need to integrate the functions for specific heat from* T_1 *to* T_2*. See "quad" from scipy.integrate.*

(c) Plot $c(T)$ for liquid water from 5-95 °C.

(d) How much thermal energy is required to raise the temperature of water from (i) 5-10 °C? and (ii) 90-95 °C?

5. **(Challenge) Adiabatic Flame Temperature:** In the same template Google Colab notebook, compute the adiabatic flame temperature at constant pressure for the ideal combustion of elemental carbon in (i) pure oxygen and (ii) air. (iii) Explain the difference you find.

   Hint: You will need to find the temperature such that $\Delta h_{rxn} = 0$*, or where* $h_{products}(T_f) = h_{reactants}(T_i)$*. This can be solved for iteratively (i.e. write code that guesses the* T_f *for computing* $h_{products}$*, solves for* T_f*, then checks to see if they match within some error. If they do not match, plug that value for* T_f *back in and repeat until they do.) or alternatively using SciPy's fminbound function.*

Resource: Thermodynamics and Climate Change

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