Kitty Wang
Thermodynamics and Climate Change
Professor P. Godart
July 11, 2022

Problem Set 2

Question 1. Concept Questions

(a) i. In a system where pressure remains constant, the heat that is released in a chemical reaction is given by the change in enthalpy between the products and reactants as $dH = dQ + VdP$. However, due to $dP = 0$, this equation applying the First Law of Thermodynamics can be simplified as $dH = dQ$ where the heat released will be equal to the change in enthalpy.

ii. The heat released in a chemical reaction can be expressed as the change in internal energy when the system maintains a constant volume. Given the application of the First Law of Thermodynamics through $dQ = dU - PdV$, since $dV = 0$, $dQ = dU$.

(b) More heat is released in a chemical reaction that occurs at constant pressure, since $c_p = c_v + R$, which indicates that c_p will always be greater than c_v, thus when we calculate the heat with $\int_{T0}^{T1} C_p T dt$, it will be greater than $\int_{T0}^{T1} C_v T dt$.

(c) The adiabatic flame temperature will be lower if air is used in combustion instead of pure oxygen as the other gaseous species present in air, such as N_2, will cause some of the energy generated by the combustion process to be allocated towards heating up those gases. The nitrogen present in air consumes a significant portion of the produced heat, thereby causing a large decrease in the final adiabatic flame temperature.

(d) Despite graphite not having any covalent bonds, its carbon atoms are still organized in a strong hexagonal ring structure comprising sheets of fused rings. As a result, when that structure is broken during combustion, it will release heat to form carbon monoxide or carbon dioxide in the process.

(e) i. Since glucose is more complex than coal, it would be expected for glucose to have a higher molar heating value since the process of its combustion results in many bonds being formed compared to the combustion of coal, which would release a greater amount of heat as a result.

ii. While glucose may be expected to have a higher molar heating value, since the combustion of glucose yields 6 CO_2 molecules, it should counterbalance the upped q_p value, thus leading to an overall higher carbon intensity.

(f) When liquid water is produced from a combustion reaction, it will yield a greater quantity of sensible heat. Because of this condensation into liquid form, all of the heating value of the reactant fuel including sensible heat and latent heat are accounted for. On the other hand, less heat is released with a reaction that produces water vapor since a significant (and non-negligible) amount of heat contributes to completing the phase change into gas and is used instead as latent heat.

Question 2. Combustion Reactions

(a) $2\,CH_3OH + 3\,(O_2 + 3.77\,N_2) \longrightarrow 2\,CO_2 + 4\,H_2O + 11.31\,N_2$
(b) $CH_4 + 2\,(O_2 + 3.77\,N_2) \longrightarrow CO_2 + 2\,H_2O + 7.54\,N_2$
(c) $C_5H_{12} + 8\,(O_2 + 3.77\,N_2) \longrightarrow 6\,H_2O + 5\,CO_2 + 30.16\,N_2$
(d) $C + (O_2 + 3.77\,N_2) \longrightarrow CO_2 + 3.77\,N_2$
(e) $2\,Mg + (O_2 + 3.77\,N_2) \longrightarrow 2\,MgO + 3.77\,N_2$

Question 3. Forming of fuels

(a) $3\,C + 4\,H_2O \longrightarrow CO_2 + 2\,CH_3OH$ $2\,CH_3OH + 3\,(O_2 + 3.77\,N_2) \longrightarrow 2\,CO_2 + 4\,H_2O + 11.31\,N_2$

(b) The thermal energy required to produce 1 kmol of methanol can be expressed as the change in enthalpy between the products and reactants, such that

$$Q = \Delta H_{formation} = H_{products} - H_{reactants}$$

Substituting the values of enthalpies of formation for each of the species yields

$$\Delta H_{formation} = (-393.5\frac{MJ}{kmol}) + 2(-238.6\frac{MJ}{kmol}) - [3(0\frac{MJ}{kmol}) + 4(-285.8\frac{MJ}{kmol})]$$

$$\Delta H_{formation} = 272.5MJ$$

for 2 kmol of methanol produced.

$\therefore$ 136.25 MJ of thermal energy is required to generate just 1 kmol of CH_3OH.

(c) In pure oxygen, the combustion of pure coal is given by

$$C + O_2 \longrightarrow CO_2$$

In addition, since carbon intensity can be expressed as the rate of the mass of CO_2 produced per unit of thermal energy released and 1 kmol of C yields 1 kmol of CO_2, we can represent this relationship as

$$\mathrm{I}_{CO_2} = \frac{m_{CO_2}}{q_p}$$

First, we must calculate the thermal energy released through the combustion reaction.

$$\mathrm{q}_p = \Delta h_{rxn} = (-393.5\frac{MJ}{kmol}) - (0\frac{MJ}{kmol} + 0\frac{MJ}{kmol})$$

$$\mathrm{q}_p = \Delta h_{rxn} = -393.5\frac{MJ}{kmol_C}$$

$$\because I_{CO_2} = \frac{m_{CO_2}}{q_p},$$

$$\mathrm{I}_{CO_2} = (\frac{1kmol_{CO_2}}{1kmol_C})(\frac{1}{q_p})$$

$$\mathrm{I}_{CO_2} = \frac{1kmol_{CO_2}}{393.5MJ}$$

$$\mathrm{I}_{CO_2} = 2.541 \cdot 10^{-3} \text{ kmol } \mathrm{CO_2/MJ}$$

(d) Following the strategy used in part(c), we can first compute the energy released by the combustion and apply the formula for carbon intensity once again

$$2\,CH_3OH + 3\,O_2 \longrightarrow 2\,CO_2 + 4\,H_2O$$

$$\mathrm{I}_{CO_2} = \frac{m_{CO_2}}{q_p}$$

$$\mathrm{q}_p = \Delta h_{rxn} = 2(-393.5\frac{MJ}{kmol}) + 4(-241.8\frac{MJ}{kmol}) - [2(-238.6\frac{MJ}{kmol}) + 3(0\frac{MJ}{kmol})]$$

$$\mathrm{q}_p = \Delta h_{rxn} = -1277\frac{MJ}{2kmol_{CH_3OH}}$$

$$\mathrm{I}_{CO_2} = (\frac{2kmol_{CO_2}}{2kmol_{CH_3OH}})(\frac{2kmol_{CH_3OH}}{1277MJ})$$

$$\mathrm{I}_{CO_2} = \frac{1kmol_{CO_2}}{638.5MJ}$$

$$\therefore I_{CO_2} = 1.566 \cdot 10^{-3} \text{ kmol } \mathrm{CO_2/MJ}$$

(e) Based on the carbon intensity calculated for both combustion processes, it appears that burning methanol may be a promising alternative to burning coal since it yields more energy per unit of CO_2 that is created as a product. Considering that methanol is only 61.6% as carbon intensive as regular coal combustion, it may be viable as a less detrimental reactant for generating energy. However, it is also critical to recognize that for every kmol of coal required for coal combustion, methanol combustion needs 2 kmol to produce 1277 MJ of energy. And although methanol production is relatively low-cost and scalable, the intermediate byproducts generated from producing methanol in the first place must also be considered.

Question 4. Exploring Heat Capacity
Please refer to the following Google Colab notebook here.

Question 5. Challenge: Adiabatic Flame Temperature
Please refer to the following Google Colab notebook here or the link above.