

Concepts and Problems from the First Law of Thermodynamics.

1. Define the First and Second Laws of Thermodynamics in words and with an equation. Discuss how they are related to our understanding on ΔH , ΔS , and ΔG .
2. Standard molar entropy (S°) can be used to calculate reaction entropies. These values are always positive ($S^\circ > 0$). Why?
3. For each pair, predict which molecule will have a higher molar entropy:

CO vs. CO₂ (both are gases at 100 °C) H₂O (s) vs. H₂O (l) CH₄ (g) at 25 °C vs. CH₄ (g) at 250 °C

4. In class, we discussed that one example of the relationship between ΔU , q , and w is a car engine. The system is represented by the car itself – the total internal energy is determined by how much gas you have in the tank. As you drive the car, work being done to move the car and the engine is getting hot – together, these are the two ways that the internal energy of the system is being transferred to the surroundings.

Now it's your turn, think about the human body. The food that you eat is your energy. Describe how your body gets rid of that energy and relate it back to $\Delta U = q + w$.

5. When thinking about the heat of a reaction, q and ΔH can be used interchangeably in most cases.
 - a. Why?
 - b. What must be true if $q \neq \Delta H$?
6. If 100 mL of liquid water is cooled from 98 °C to 25 °C:
 - a. Is the reaction endothermic or exothermic?
 - b. What is the sign of ΔH ?
 - c. What is the sign of ΔS ?
 - d. The heat capacity of liquid water is 4.184 J g⁻¹ °C⁻¹. Calculate ΔH . Recall that the density of water is 1 g/mL.

7. Octane (C_8H_{18}) has a melting temperature of $-57.1\text{ }^\circ\text{C}$ and a boiling temperature of $125.1\text{ }^\circ\text{C}$.
- a. ΔH_{vap} for octane is 36.3 kJ/mol . Calculate ΔS_{vap} . *Hint: remember that $\Delta G = 0$ at the phase change temperature.*
- b. If exactly 12.2 g of octane vapor at $125.1\text{ }^\circ\text{C}$ is cooled to a solid at the melting temperature, calculate ΔH . $\Delta H_{\text{fus}} = 21.75\text{ kJ/mol}$ $C_{\text{liquid}} = 255.68\text{ J mol}^{-1}\text{ }^\circ\text{C}^{-1}$. All other info is above.

8. Consider the sublimation of sodium metal: $\text{Na (s)} \rightleftharpoons \text{Na (g)}$
- Write an equilibrium constant for this reaction.
 - Predict the sign of ΔH and ΔS . Clearly explain why you made these selections.
 - Will this reaction be spontaneous at high temperatures, low temperatures, both, or neither?
 - Noting that $\Delta H_f^0 = 107.5 \text{ kJ mol}^{-1}$ and $\Delta G_f^0 = 77.0 \text{ kJ mol}^{-1}$ for Na (g), determine ΔH° , ΔG° , and ΔS° for this reaction. *Hint: what is special about Na(s) and what does that mean about the formation energies?*
 - From this information, calculate the sublimation temperature of sodium. *Hint: remember that $\Delta G = 0$ at the phase change temperature.*
 - Calculate the equilibrium constant for this reaction.
 - What pressure of sodium is needed for equilibrium to be established?
 - If the pressure of Na (g) is 5×10^{-10} atm, will the equilibrium shift to make more gas or solid?
 - The heat capacity of Na(s) is $1.214 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$. If a block of Na (s) at $350 \text{ }^\circ\text{C}$ is placed in 300 mL of mineral oil (density = 0.85 g/mL and $C = 1.67 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$) at $20 \text{ }^\circ\text{C}$ and the final temperature is found to be $32 \text{ }^\circ\text{C}$, what was the mass of sodium?

9. The combustion of octane produces -5.53 MJ/mol of heat. If 100 g of octane is combusted, how much water at $25 \text{ }^\circ\text{C}$ can be boiled?

This is a big problem – let's walk through it stepwise:

Determine how much heat is produced when 100 g of octane is combusted. You'll need a balanced equation, the moles of octane, and use ΔH as a conversion factor to figure out the enthalpy for this reaction.

Ok, now figure out how many the heat that it would take exactly one mole of H_2O to be heated from a liquid at $25 \text{ }^\circ\text{C}$ to a gas at the boiling temperature. Do this in two step: 1. How much heat to boil 1 mole of water? 2. How much heat to increase the temperature from 25°C to $100 \text{ }^\circ\text{C}$? ΔH_{vap} of water is 40.65 kJ/mol and in a previous problem, you learned that the heat capacity of liquid water is $4.184 \text{ J g}^{-1} \text{ }^\circ\text{C}^{-1}$. Your answer to this part will be in J per 1 mol (which we can use as a conversion factor for the next part).

Ok, from the 1st part, you found out how much energy is produced and the second part you learned how much energy is needed for exactly one mole. Now use the answer to the 2nd part as a conversion factor to convert the first answer to moles.