

CH301 Worksheet 11 (Answer Key)

1. What is the second law of thermodynamics? How does this apply to someone exploding a hydrogen balloon? $2 \text{ H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{ H}_2\text{O}(\text{g})$

The second law of thermodynamics states that the entropy of the universe is always increasing. This reaction appears to violate this law because the entropy in 2 moles of gaseous water is less than the entropy of 3 moles of gaseous hydrogen and oxygen. However, the reaction also releases heat, and this extra heat can contribute to entropy in the surroundings. In other words, the entropy of the system decreases, but the entropy of the surroundings increases, and the entropy of the universe increases.

2. Let's talk about signs. What does a positive or negative value mean for change in enthalpy (ΔH), work (w), and change in Gibbs free energy (ΔG)? Remember, be the system! And try to do this one from memory. Don't just copy it directly from the notes.

A positive value for ΔH means that the system is absorbing heat, and the reaction is endothermic.

A negative value for ΔH means that the system is losing heat, and the reaction is exothermic.

A positive value for w means that work is being done on the system (the surroundings are doing work on the system).

A negative value for w means that work is being done by the system (the system is doing work on the surroundings). After pressure is removed, the gas inside a balloon can do work on the surroundings to increase the volume.

Try explaining this one to your peers a couple times. It will help you remember the significance of the sign.

3. A bomb calorimeter is filled with 2 L of water. After a reaction, the temperature of the water raises from 25.0 °C to 28.3 °C. The density and heat capacity of water are 1 g/mL and 4.184 J/(g·K), respectively. The heat capacity of the calorimeter is 85 J per K.

Determine ΔH of the reaction.

$$m = 2000 \text{ mL} \cdot 1 \text{ g/mL} = 2000 \text{ g}$$

$$C_w = 4.184 \text{ J/(g}\cdot\text{K)}$$

$$\Delta T = 301.3 \text{ K} - 298 \text{ K} = 3.3 \text{ K}$$

$$C_{\text{cal}} = 85 \text{ J/K}$$

$$\Delta H = m \cdot C_{\text{liq}} \cdot \Delta T + C_{\text{cal}} \cdot \Delta T = 2000 \text{ g} \cdot 4.184 \text{ J/(g}\cdot\text{K)} \cdot 3.3 \text{ K} + 85 \text{ J/K} \cdot 3.3 \text{ K} = 27894.9 \text{ J}$$

4. The same bomb calorimeter is filled with 2 L of a liquid that has a density of 1.7 grams per mL. A reaction releases 250 kJ of heat, and the temperature of the liquid increases from 25 °C to 27 °C. What is the heat capacity of the liquid?

$$\Delta H = 250 \text{ kJ} = 250,000 \text{ J}$$

$$d = 1.7 \text{ g/mL}$$

$$V = 2 \text{ L}$$

$$m = 2000 \text{ mL} \cdot 1.7 \text{ g/mL} = 3400 \text{ g}$$

$$\Delta T = 300 \text{ K} - 298 \text{ K} = 2 \text{ K}$$

$$C_{\text{cal}} = 85 \text{ J/K}$$

$$\Delta H = m \cdot C_{\text{liq}} \cdot \Delta T + C_{\text{cal}} \cdot \Delta T$$

$$C_{\text{liq}} = [\Delta H - C_{\text{cal}} \cdot \Delta T] / [m \cdot \Delta T] = [250000 \text{ J} - (85 \text{ J/K} \cdot 2 \text{ K})] / [3400 \text{ g} \cdot 2 \text{ K}] = 36.7 \text{ J/(g}\cdot\text{K)}$$

5. The liquid is allowed to cool down to 25 °C. The calorimeter is equipped with another reaction that releases 400 kJ of heat. What is the final temperature of the liquid after the reaction is complete?

$$T_i = 298 \text{ K}$$

$$\Delta H = 400,000 \text{ J}$$

$$m = 3400 \text{ g}$$

$$C_{\text{cal}} = 85 \text{ J/K}$$

$$C_{liq} = 36.7 \text{ J/(g}\cdot\text{K)}$$

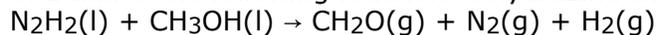
$$\Delta H = m \cdot C_{liq} \cdot \Delta T + C_{cal} \cdot \Delta T$$

$$\Delta T = \Delta H / [m \cdot C_{liq} + C_{cal}] = 400,000 \text{ J} / [3400 \text{ g} \cdot 36.7 \text{ J/(g}\cdot\text{K)} + 85 \text{ J/K}] = 3.2 \text{ K}$$

$$\Delta T = T_f - T_i$$

$$T_f = \Delta T + T_i = 3.2 \text{ K} + 298 \text{ K} = 301.2 \text{ K} = 28.2 \text{ }^\circ\text{C}$$

6. Balance the following reaction of hydrazine with methanol. Calculate the work done.



$$\Delta n_{\text{gas}} = 4 \text{ mol} - 0 \text{ mol} = 4 \text{ mol}$$

$$w = -\Delta n_{\text{gas}} \cdot R \cdot T = -4 \text{ mol} \cdot 8.314 \text{ J/(K}\cdot\text{mol)} \cdot 298 \text{ K} = -9.9 \text{ kJ}$$

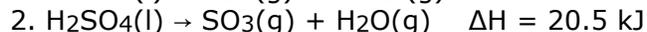
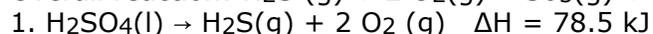
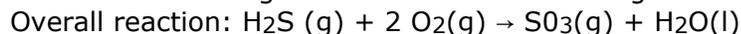
7. If the work done on a system is 5.7 kJ, and the external pressure is equal to 3.5 atm. Is the volume of the system increasing or decreasing?

Because work is being done on the system, the sign of the work is positive. Also, $w = -P\Delta V$. Because P is positive, ΔV must be negative for the work to be positive. So, the volume must be decreasing.

8. In your own words, what is Hess's Law?

Hess's law states that the change in energy of one reaction is equal to the sum of the changes in energy required for all the smaller steps that can complete the reaction. This law is why we can use the enthalpies of formation for reactants and products to calculate the overall change in enthalpy.

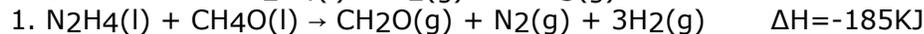
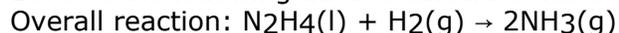
9. Use the following data to calculate the change in enthalpy.



The overall reaction is equal to the reverse of reaction 1 plus the forwards reactions of reactions 2 and 3.

$$\Delta H_{\text{total}} = -\Delta H_1 + \Delta H_2 + \Delta H_3 = -78.5 \text{ kJ} + 20.5 \text{ kJ} - 11 \text{ kJ} = -69 \text{ kJ}$$

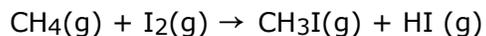
10. Use the following data to calculate the change in enthalpy.



The overall reaction is equal to the sum of the forward reactions 1 and 2 and the reverse reaction of 3.

$$\Delta H_{\text{total}} = \Delta H_1 + \Delta H_2 - \Delta H_3 = -185 \text{ kJ} - 230 \text{ kJ} + 325 \text{ kJ} = -90 \text{ kJ}$$

11. Determine the ΔH_{rxn} for the reaction using the provided bond energies:



Bond energies:

$$\text{C-H} : 416 \text{ kJ/mol} \quad \text{H-I} : 299 \text{ kJ/mol}$$

$$\text{I-I} : 151 \text{ kJ/mol} \quad \text{C-I} : 213 \text{ kJ/mol}$$

Is the reaction endothermic or exothermic?

$\Delta H_{\text{rxn}} = \text{sum of bond energies of reactants} - \text{sum of bond energies of products}$

$$\Delta H_{\text{rxn}} = [4(\text{C-H}) + 1(\text{I-I})] - [3(\text{C-H}) + 1(\text{C-I}) + 1(\text{H-I})]$$

$$\Delta H_{\text{rxn}} = [4(416 \text{ kJ/mol}) + (151 \text{ kJ/mol})] - [3(416 \text{ kJ/mol}) + (213 \text{ kJ/mol}) + (299 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}} = +55 \text{ kJ/mol}$$

The reaction is endothermic because ΔH_{rxn} is positive.

12. Determine the boiling point for iron. $\Delta H_{\text{vap}} = 349.6 \text{ kJ/mol}$ and $\Delta S_{\text{vap}} = 111.55 \text{ J/(mol}\cdot\text{K)}$

Phase changes are equilibrium processes, hence $\Delta G = 0$ and $\Delta H = T\Delta S$

$$T = \Delta H/\Delta S = (349.6 \text{ kJ/mol}) / (.11155 \text{ kJ/(mol}\cdot\text{K)}) = 3134 \text{ K}$$

Note: make sure you put entropy and enthalpy both in either kJ or J.

13. Calculate the amount of heat given off when 11 grams of manganese (Mn) is oxidized to $\text{Mn}_2\text{O}_3(\text{s})$ at standard state conditions. $\Delta H_{\text{f},\text{Mn}_2\text{O}_3(\text{s})} = -962.3 \text{ kJ/mol}$



$$\Delta H_{\text{f},\text{Mn}} = 0 \text{ kJ/mol}$$

$$\Delta H_{\text{f},\text{O}_2(\text{g})} = 0 \text{ kJ/mol}$$

$$\Delta H_{\text{rxn}} = \sum \Delta H_{\text{f},\text{products}} - \sum \Delta H_{\text{f},\text{reactants}}$$

$$\Delta H_{\text{rxn}} = \Delta H_{\text{f},\text{Mn}_2\text{O}_3}$$

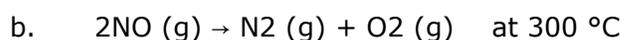
$$q = (-962.3 \text{ kJ/mol Mn}_2\text{O}_3)(1 \text{ mol Mn}_2\text{O}_3 / 2 \text{ mol Mn})(1 \text{ mol Mn} / 55 \text{ g Mn})(11 \text{ g Mn})$$

$$q = -96.4 \text{ kJ}$$

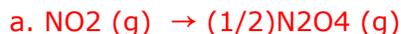
96.4 kJ of heat released.

Note: be careful with the sign. The question asks how much heat was released, the negative is therefore implied.

14. Calculate the work done on the systems with only one mole of reactant:



$$w = -P\Delta V = -\Delta nRT$$



$$T = 30^\circ\text{C} + 273 = 303\text{K}$$

$$\Delta n = .5 \text{ mol} - 1 \text{ mol} = -.5 \text{ mol gas}$$

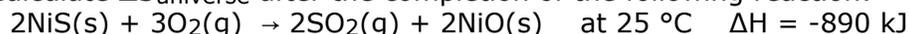
$$w = -(-.5 \text{ mol gas})(8.3145 \text{ J/K mol})(303 \text{ K})(1 \text{ kJ} / 1000\text{J}) = 1.25 \text{ kJ}$$



$$\Delta n = 1 \text{ mol} - 1 \text{ mol} = 0 \text{ mol}$$

$$w = 0 \text{ kJ}$$

15. Calculate $\Delta S_{\text{universe}}$ after the completion of the following reaction:



Substance S(J/Kmole)

SO_2 248

NiO 38

O_2 205

NiS 53

$$\Delta S_{\text{sys}} = [2(248) + 2(38)] - [2(53) + 3(205)] = -149 \text{ J/K}$$

$$\Delta S_{\text{surr}} = -\Delta H/T = -(-890 \text{ kJ})/298 \text{ K} = 3 \text{ kJ/K}$$

$$\Delta S_{\text{universe}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -149 \text{ J/K} + 3000 \text{ J/K} = 2851 \text{ J/K}$$

16. Determine the ΔG when:

$$\Delta S_{\text{universe}} = 1303 \text{ J/K}$$

$$\Delta S_{\text{surr}} = 1.300 \text{ kJ/K}$$

$$T = 25^\circ\text{C}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$$

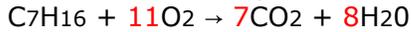
$$\Delta S_{\text{sys}} = \Delta S_{\text{univ}} - \Delta S_{\text{surr}} = 1303 \text{ J/K} - 1300 \text{ J/K} = 3 \text{ J/K}$$

$$\Delta S_{\text{surr}} = -\Delta H/T$$

$$\Delta H = -T\Delta S_{\text{surr}} = -(298\text{K})(1.3 \text{ kJ/K}) = -387.4 \text{ kJ}$$

$$\Delta G = \Delta H - T\Delta S_{\text{sys}} = -387.4 \text{ kJ} - (298\text{K})(.00305 \text{ kJ/K}) = 388.3 \text{ kJ}$$

17. Balance the following combustion reaction and determine the ΔH_{rxn} .



Bond Energies

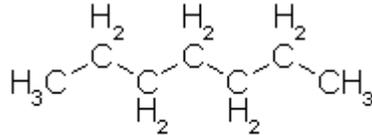
C-C: 346 kJ/mol O=O: 498 kJ/mol

C-H: 413 kJ/mol C=O: 799 kJ/mol

H-O: 463 kJ/mol C-O: 358 kJ/mol

O-O: 146 kJ/mol

If the reaction is carried out at 25 °C what is the ΔS_{surr} ?



$\Delta H_{\text{rxn}} = \text{sum of bond energies of reactants} - \text{sum of bond energies of products}$

$$\Delta H_{\text{rxn}} = [6(\text{C-C}) + 16(\text{C-H}) + 11(\text{O=O})] - [7(2)(\text{C=O}) + 8(2)(\text{H-O})]$$

$$\Delta H_{\text{rxn}} = [(346 \text{ kJ/mol}) + 16(413 \text{ kJ/mol}) + 11(498 \text{ kJ/mol})] - [7(2)(799 \text{ kJ/mol}) + 8(2)(463 \text{ kJ/mol})]$$

$$\Delta H_{\text{rxn}} = -4432 \text{ kJ/mol}$$

$$\Delta S_{\text{surr}} = -\Delta H/T = -(-4432 \text{ kJ/mol})/298\text{K} = 14.87 \text{ kJ/K}$$

18. Determine the minimum temperature for a reaction with $\Delta H = 271 \text{ kJ}$ and $\Delta S = 195 \text{ J/K}$ to be spontaneous.

When $\Delta G = 0$ the reaction is at equilibrium, so solve for T under these conditions.

$$\Delta G = \Delta H - T\Delta S = 0$$

$$T = \Delta H/\Delta S = 271 \text{ kJ} / (0.195 \text{ kJ/K}) = 1389.74 \text{ K}$$

19. Consider the reaction: $\text{CO(g)} + \text{Cl}_2(\text{g}) \rightarrow \text{COCl}_2(\text{g})$

Calculate ΔG_{rxn} at 25 °C

Substance	ΔH_f (kJ/mol)	S (J/ mol K)
CO	-110.5	197.6
Cl ₂	0.0	223.0
COCl ₂	-223.0	289.2

$$\Delta H_{\text{rxn}} = \sum \Delta H_{f,\text{products}} - \sum \Delta H_{f,\text{reactants}}$$

$$\Delta H_{\text{rxn}} = [-223 \text{ kJ/mol}] - [-110.5 \text{ kJ/mol}] = -112.5 \text{ kJ/mol}$$

$$\Delta S_{\text{rxn}} = \sum \Delta S_{m,\text{products}} - \sum \Delta S_{m,\text{reactants}}$$

$$\Delta S_{\text{rxn}} = [289.2 \text{ J/mol K}] - [(223 \text{ J/mol K}) + (197.6 \text{ J/mol K})] = -131.4 \text{ J/ mol K}$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = -112.5 \text{ kJ/mol} - 298\text{K}(-0.1314 \text{ kJ/mol K}) = -72.34 \text{ kJ/mol}$$

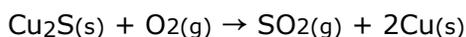
20. Determine ΔG_f for $\text{SO}_2(\text{g})$. Assume 25 °C for all reactions.

$$\Delta H_{f,\text{SO}_2}(\text{g}) = -297 \text{ kJ/mol}$$

$$S_{m,\text{SO}_2}(\text{g}) = 248 \text{ J/(K mol)}$$

Then determine ΔG_{rxn} of the following reaction:

$$\Delta G_f \text{ Cu}_2\text{S}(\text{s}) = -86.2 \text{ kJ/mol}$$



$$\Delta G_{f,\text{SO}_2} = \Delta H - T\Delta S = (-297 \text{ kJ/mol}) - (298\text{K})(.248 \text{ kJ/mol}) = -370.9 \text{ kJ/mol}$$

$$\Delta G_{\text{rxn}} = \sum \Delta G_{f,\text{products}} - \sum \Delta G_{f,\text{reactants}}$$

$$\Delta G_{\text{rxn}} = -379.9 \text{ kJ/mol} - (-86.2 \text{ kJ/mol}) = -284.7 \text{ kJ/mol}$$