CH302: Worksheet 1c Answer key. Examples of Advanced Thermo listed by question type.

• Hess's Law and combined reaction enthalpies

1. Given that

 $\begin{array}{l} S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)} \, \Delta H = -296.8 \ kJ/mol\\ S_{(s)} + 3/2 \ O_{2(g)} \rightarrow SO_{3(g)} \, \Delta H = -395.6 \ kJ/mol,\\ \mbox{determine the enthalpy change for the decomposition reaction}\\ 2SO_{3(g)} \rightarrow 2SO_{2(g)} + O_{2(g)}. \end{array}$

Answer: Multiply top equation by 2 and bottom equation by -2. The answer for Δ Hrxn = (2 x -296.8) + (-2 x -395.6) = 197.6kJ

2. Given that

 $\begin{array}{c} 2H_2 + O_2 \rightarrow 2H_2O \ \Delta H = -571.6 \ \text{kJ/mol} \\ C_3H_4 + 4O_2 \rightarrow 3CO_2 + 2H_2O \ \Delta H = -1937 \ \text{kJ/mol} \\ C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O \ \Delta H = -2220 \ \text{kJ/mol}, \\ \text{determine the heat of the reaction for} \\ C_3H_4 + 2H_2 \rightarrow C_3H_8. \end{array}$

Answer: Multiply the bottom equation by -1. Everything then cancels. The answer for Δ Hrxn = (-571.6) + (-1937) + (-1 x -2220) = -288.6 kJ

• Internal Energy calculations

3. The standard molar heat of freezing for water is -6020 J/mol. Calculate q, w, and ΔE for freezing 1.0 mol of water at 0°C and 1 atm pressure. (Hint: there is no need to use a calculator.)

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Answer:

q = -6020 \text{ J/mol}

w = 0 \text{ (no gas involved)}

\Delta E = q + w = -6020 \text{ J/mol}
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4. For a reaction in which more moles of gas are produced than are consumed (at constant pressure), ΔH is

- a) Equal to ΔE
- b) Less than ΔE
- c) Greater than ΔE correct from equation $\Delta H = \Delta E + P\Delta V$ since P ΔV will be positive

• Statistical thermodynamics: internal energy theory

5. What is the total motional contribution to the molar internal energy of CO₂? (Express your answer in amounts of RT.)

Answer: 3/2RT + 2/2RT = 5/2RT for linear molecule

6. What is the total motional contribution to the molar internal energy of NH₃? (Express your answer in Amounts of RT.)

Answer: 3/2RT + 3/2RT = 3RT for linear molecule

• Calculation of the entropy change at a phase transition

8. What is the entropy change for the freezing of 3.33 grams of an alcohol, C_2H_3OH , at 373.2K given that $\Delta H = -40,700 \text{ J/mol}$?

Answer: $\Delta G = \Delta H - T\Delta S$ but $\Delta G = 0$ for a phase transition so $\Delta H = T\Delta S$. Substitute T = 373.2K and -40700 J/mol to find $\Delta S = -109$ J/K for one mole. The question is ambiguous about the quantity of loohol so I am finding ΔS per mole so I don't have to do any more work.

• Statistical thermodynamics: Boltzmann formula

- 9. Use the Boltzmann formula to calculate the entropy at T = 0 for
 - a) a mole of BCl₃ that can be oriented one way
 - b) a mole of BCl₂Br that can be oriented three ways

Answer:

a) S = 0 because there is only one orientation and $\ln 1$ will = 0 in the equation $S = k \ln W$ no matter how many molecules.

b) $S = 1.38 \times 10^{-23} \ln 3^{6.02 \times 1023} = 9.1 \text{ J/Kmole}$

• Statistical thermodynamics: Third Law

10. Based on the structures of each of the following molecules, which are most likely to have a residual energy in their crystal forms at T = 0?

a) CO_2 b) O_3 c) HCl d) Cl_2 Answer: O_3 and HCl have residual entropy because they have more than one orientation. Symmetrical CO_2 and

 Cl_2 do not and have S = 0.

• Entropy Change and the surrounding

11. When a sugar cube dissolves in a cup of coffee (an endothermic process), what the the signs of the entropy change for the system, surroundings and universe, respectively.

a) -,-,-

b) -,+,+

c) +,-,+ correct. The system is getting more disordered and the universe must get more disordered because of second law.

d) +,+,+

e) none are correct

• Calculating the change in free energy

12. Calculate ΔG° for the reaction $2N_2(g) + 3O_3(g) \rightarrow 2 N_2O_3(g)$ at $25^{\circ}C$

	ΔH_{f}^{o}	S ^o
N ₂	0	191.5
03	0	205
N ₂ O ₃	83.72	312.2

a) 540 kJ/mol rxn

b) 278.7 kJ/mol rxn

- c) -561 kJ/mol rxn
- d) -540 kJ/mol rxn
- e) +56 kJ/mol rxn

Answer: Calculate $\Delta H = 167$ kJ and $T\Delta S = 111$ kJ. So $\Delta H - T\Delta S = \Delta G = 56$ kJ.