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

## - Hess's Law and combined reaction enthalpies

1. Given that

$$
\mathrm{S}_{(\mathrm{s})}+\mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{SO}_{2(\mathrm{~g})} \Delta \mathrm{H}=-296.8 \mathrm{~kJ} / \mathrm{mol}
$$

$\mathrm{S}_{(\mathrm{s})}+3 / 2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{SO}_{3(\mathrm{~g})} \Delta \mathrm{H}=-395.6 \mathrm{~kJ} / \mathrm{mol}$,
determine the enthalpy change for the decomposition reaction $2 \mathrm{SO}_{3(\mathrm{~g})} \rightarrow 2 \mathrm{SO}_{2(\mathrm{~g})}+\mathrm{O}_{2(\mathrm{~g})}$.

Answer: Multiply top equation by 2 and bottom equation by -2 .
The answer for $\Delta \operatorname{Hrxn}=(2 \mathrm{x}-296.8)+(-2 \mathrm{x}-395.6)=197.6 \mathrm{~kJ}$
2. Given that

$$
\begin{aligned}
& 2 \mathrm{H}_{2}+\mathrm{O}_{2} \rightarrow 2 \mathrm{H}_{2} \mathrm{O} \Delta \mathrm{H}=-571.6 \mathrm{~kJ} / \mathrm{mol} \\
& \mathrm{C}_{3} \mathrm{H}_{4}+4 \mathrm{O}_{2} \rightarrow 3 \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O} \Delta \mathrm{H}=-1937 \mathrm{~kJ} / \mathrm{mol} \\
& \mathrm{C}_{3} \mathrm{H}_{8}+5 \mathrm{O}_{2} \rightarrow 3 \mathrm{CO}_{2}+4 \mathrm{H}_{2} \mathrm{O} \Delta \mathrm{H}=-2220 \mathrm{~kJ} / \mathrm{mol}
\end{aligned}
$$

determine the heat of the reaction for
$\mathrm{C}_{3} \mathrm{H}_{4}+2 \mathrm{H}_{2} \rightarrow \mathrm{C}_{3} \mathrm{H}_{8}$.
Answer: Multiply the bottom equation by -1 . Everything then cancels.
The answer for $\Delta \operatorname{Hrxn}=(-571.6)+(-1937)+(-1 \mathrm{x}-2220)=-288.6 \mathrm{~kJ}$

## - Internal Energy calculations

3. The standard molar heat of freezing for water is $-6020 \mathrm{~J} / \mathrm{mol}$. Calculate $\mathrm{q}, \mathrm{w}$, and $\Delta \mathrm{E}$ for freezing 1.0 mol of water at $0^{\circ} \mathrm{C}$ and 1 atm pressure. (Hint: there is no need to use a calculator.)

Answer:
$\mathrm{q}=-6020 \mathrm{~J} / \mathrm{mol}$
$\mathrm{w}=0$ (no gas involved)
$\Delta \mathrm{E}=\mathrm{q}+\mathrm{w}=-6020 \mathrm{~J} / \mathrm{mol}$
4. For a reaction in which more moles of gas are produced than are consumed (at constant pressure), $\Delta \mathrm{H}$ is
a) Equal to $\Delta \mathrm{E}$
b) Less than $\Delta \mathrm{E}$
c) Greater than $\Delta \mathrm{E}$ correct from equation $\Delta H=\Delta E+P \Delta V$ since $P \Delta V$ will be positive

## - Statistical thermodynamics: internal energy theory

5. What is the total motional contribution to the molar internal energy of $\mathrm{CO}_{2}$ ? (Express your answer in amounts of RT.)

Answer: $3 / 2 \mathrm{RT}+2 / 2 \mathrm{RT}=5 / 2 \mathrm{RT}$ for linear molecule
6. What is the total motional contribution to the molar internal energy of $\mathrm{NH}_{3}$ ? (Express your answer in Amounts of RT.)

Answer: $3 / 2 \mathrm{RT}+3 / 2 \mathrm{RT}=3 \mathrm{RT}$ 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, $\mathrm{C}_{2} \mathrm{H}_{3} \mathrm{OH}$, at 373.2 K given that $\Delta \mathrm{H}=$ -40,700 J/mol?
Answer: $\Delta \mathrm{G}=\Delta \mathrm{H}-\mathrm{T} \Delta \mathrm{S}$ but $\Delta \mathrm{G}=0$ for a phase transition so $\Delta \mathrm{H}=\mathrm{T} \Delta \mathrm{S}$. Substitute $\mathrm{T}=373.2 \mathrm{~K}$ and -40700 $\mathrm{J} / \mathrm{mol}$ to find $\Delta \mathrm{S}=-109 \mathrm{~J} / \mathrm{K}$ for one mole. The question is ambiguous about the quantity of lcohol so I am finding $\Delta \mathrm{S}$ 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 $\mathrm{T}=0$ for
a) a mole of $\mathrm{BCl}_{3}$ that can be oriented one way
b) a mole of $\mathrm{BCl}_{2} \mathrm{Br}$ that can be oriented three ways

Answer:
a) $\mathrm{S}=0$ because there is only one orientation and $\ln 1$ will $=0$ in the equation $\mathrm{S}=\mathrm{k} \ln \mathrm{W}$ no matter how many molecules.
b) $\mathrm{S}=1.38 \times 10^{-23} \ln 3^{6.02 \times 1023}=9.1 \mathrm{~J} /$ 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 $\mathrm{T}=0$ ?
a) $\quad \mathrm{CO}_{2} \quad$ b) $\quad \mathrm{O}_{3}$
c) $\quad \mathrm{HCl}$
d) $\quad \mathrm{Cl}_{2}$

Answer: $\mathrm{O}_{3}$ and HCl have residual entropy because they have more than one orientation. Symmetrical $\mathrm{CO}_{2}$ and $\mathrm{Cl}_{2}$ do not and have $\mathrm{S}=0$.

## - 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 $\Delta \mathrm{G}^{0}$ for the reaction $2 \mathrm{~N}_{2}(\mathrm{~g})+3 \mathrm{O}_{3}(\mathrm{~g}) \rightarrow 2 \mathrm{~N}_{2} \mathrm{O}_{3}(\mathrm{~g})$ at $25^{\circ} \mathrm{C}$

|  | $\Delta H_{f}{ }^{\circ}$ | $S^{0}$ |
| :--- | :--- | :--- |
| $\mathrm{~N}_{2}$ | 0 | 191.5 |
| $\mathrm{O}_{3}$ | 0 | 205 |
| $\mathrm{~N}_{2} \mathrm{O}_{3}$ | 83.72 | 312.2 |

a) $540 \mathrm{~kJ} / \mathrm{mol} \mathrm{rxn}$
b) $278.7 \mathrm{~kJ} / \mathrm{mol} \mathrm{rxn}$
c) $-561 \mathrm{~kJ} / \mathrm{mol} \mathrm{rxn}$
d) $-540 \mathrm{~kJ} / \mathrm{mol} \mathrm{rxn}$
e) $+56 \mathrm{~kJ} / \mathrm{mol} \mathrm{rxn}$

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

