

Recitation Worksheet 4: Spontaneity, Entropy, and Free Energy (17.1 – 17.7)

Name:

key

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Instructions:

- Please enter your first and last name as it appears on the eLC classlist (do not use a nickname).
- Your UGA myID is a combination of letters and numbers (example: Dr. Abdelrahman MyID is ema88805).
Do not use your 81x number.
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 - If you are using an app to annotate the worksheet, make sure the pages are in the correct order and have the same layout as the original or Gradescope will not be able to read it.
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- Answers must be written in the corresponding answer box, or no credit will be awarded.
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- In which of the following reactions will result in an increase in entropy? Select all that apply. Insert letters without spaces in the answer box, example **ABCD**.

OFG

- $\Delta S > 0$
- ~~A.~~ $\text{CaO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Ca(OH)}_2\text{(s)}$
~~B.~~ $\text{Si(s)} + 2 \text{Cl}_2\text{(g)} \rightarrow \text{SiCl}_4\text{(g)}$ 3 mol, 1 mol
~~C.~~ $\text{CuSO}_4 \cdot 3 \text{H}_2\text{O(s)} + 2 \text{H}_2\text{O(g)} \rightarrow \text{CuSO}_4 \cdot 5 \text{H}_2\text{O(s)}$ 2 mol, 0 mol (g)
~~D.~~ $\text{C}_6\text{H}_6\text{(l)} + \frac{15}{2} \text{O}_2\text{(g)} \rightarrow 6 \text{CO}_2\text{(g)} + 3 \text{H}_2\text{O(g)}$ 7.5 mol, 9 mol
~~E.~~ $2 \text{H}_2\text{S(g)} + 3 \text{O}_2\text{(g)} \rightarrow 2 \text{H}_2\text{O(g)} + 2 \text{SO}_2\text{(g)}$ (not balanced) 5 mol, 4 mol
~~F.~~ $\text{CCl}_4\text{(l)} \rightarrow \text{CCl}_4\text{(g)}$
~~G.~~ $2 \text{HgO(s)} \rightarrow 2 \text{Hg(l)} + \text{O}_2\text{(g)}$ 0 mol (s), 1 mol (g)

Solid < Liquid < Gas

Increase in Entropy →

- ~~A.~~ 1 mole liquid ($\text{H}_2\text{O(l)}$) converts to solid $\therefore \Delta S < 0$
~~B.~~ ↓ in # of moles of gas $\therefore \Delta S < 0$
~~C.~~ same as B
~~D.~~ ↑ in # of moles of gas $\therefore \Delta S > 0$
~~E.~~ ↓ in # of moles of gas $\therefore \Delta S < 0$
~~F.~~ liquid phase changes to a gas phase $\therefore \Delta S > 0$
~~G.~~ 1 mol of gas produced $\therefore \Delta S > 0$

2. Which of the reactions below will be spontaneous at **only at low temperatures**? Select all that apply. Insert letters without spaces in the answer box, example **ABCD**.

ADE

- (A) $2 \text{CO(g)} + \text{O}_2\text{(g)} \rightarrow 2 \text{CO}_2\text{(g)}$ $\Delta H_{\text{rxn}} = -566.0 \text{ kJ/mol}$ $\Delta S < 0$
 (B) $2 \text{NO}_2\text{(g)} \rightarrow 2 \text{NO(g)} + \text{O}_2\text{(g)}$ $\Delta H_{\text{rxn}} = +1131.1 \text{ kJ/mol}$ $\Delta S > 0$ } spontaneous only at high temperatures
 (C) $\text{NH}_4\text{CO}_2\text{NH}_2\text{(s)} \rightarrow 2 \text{NH}_3\text{(g)} + \text{CO}_2\text{(g)}$ $\Delta H_{\text{rxn}} = +159.2 \text{ kJ/mol}$ $\Delta S > 0$
 (D) $\text{PCl}_3\text{(g)} + \text{Cl}_2\text{(g)} \rightarrow \text{PCl}_5\text{(g)}$ $\Delta H_{\text{rxn}} = -87.9 \text{ kJ/mol}$
 (E) $\text{NO(g)} + \frac{1}{2} \text{Cl}_2\text{(g)} \rightarrow \text{NOCl(g)}$ $\Delta H_{\text{rxn}} = -38.54 \text{ kJ/mol}$ $\therefore \Delta S < 0$

For a reaction to be spontaneous only at low temperatures, the system will not be entropically favorable ($\Delta S < 0$ $\therefore +T\Delta S$) & negative value of the enthalpy will overcome the positive value of $+T\Delta S$

Tip: when spontaneity is temperature dependent, the sign for ΔH & ΔS are usually the same (either both + or both are negative)

3. Calculate the entropy change in the surroundings that occur when 35.0 g of acetone (molar mass = 58.08 g/mol) condenses at its normal boiling point (56.1 °C). ΔH_{vap} of acetone is 29.1 kJ/mol. Keep your answer to 3 sig figs.

53.3

J/K

obtaining a positive value for entropy confirms that when heat is released due to the condensation of acetone increases the entropy of the surroundings

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T} = -\frac{q_{\text{sys}}}{T}$$

$$= -\frac{(-\Delta H_{\text{cond}} \times \text{mol})}{T}$$

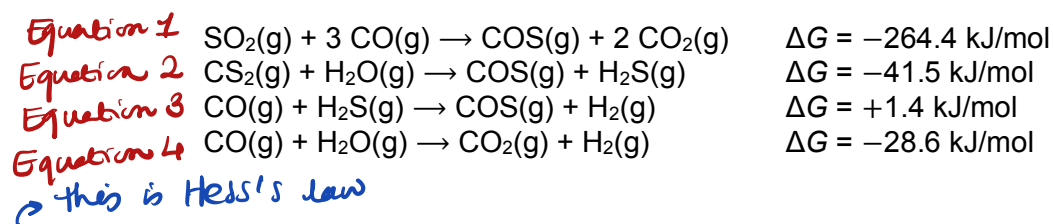
$$= -\frac{(-2.91 \times 10^4 \frac{\text{J}}{\text{mol}} \times 35.0 \text{ g acetone} \times \frac{1 \text{ mol acetone}}{58.08 \text{ g}})}{(56.1 + 273.15) \text{ K}}$$

$$= 53.260917 \text{ J/K}$$

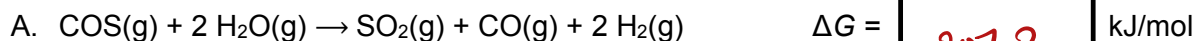
$$\sim 53.3 \text{ J/K}$$

Condensation is an exothermic process
 $\therefore \Delta H_{\text{vap}} = -\Delta H_{\text{cond}}$
 $\text{gas} \rightleftharpoons \text{liquid}$ condensation

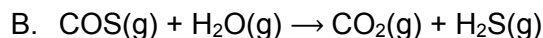
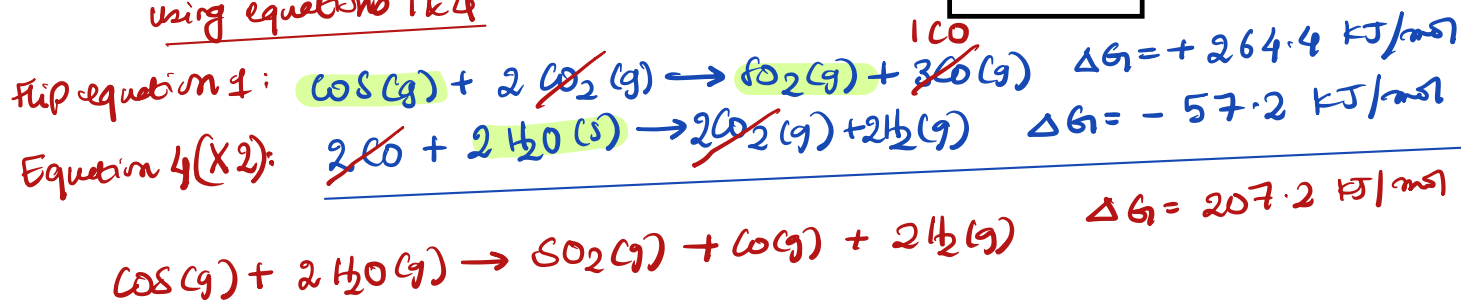
4. You are given a list of reactions below along with ΔG values. Keep your answers to one decimal place.



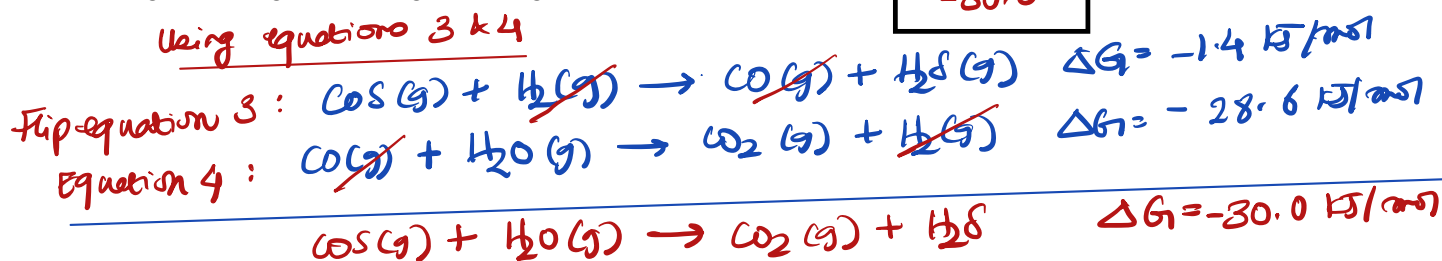
Combine the equations as necessary to obtain ΔG values for the following reactions:



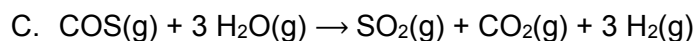
using equations 1 & 4



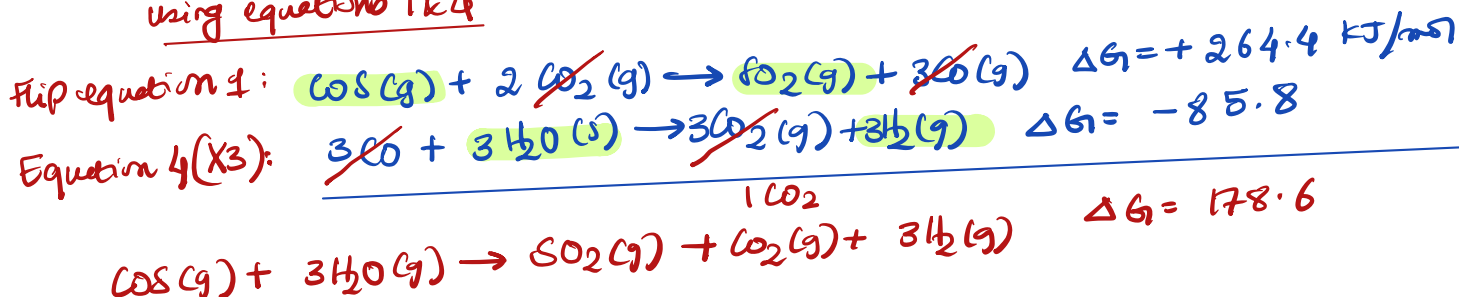
using equations 3 & 4



Same as part A but instead multiply equation 4 times 3



using equations 1 & 4



5. Which of the following has the substance with the greater entropy listed first? Select all that apply.
Insert letters without spaces in the answer box, example **ABCD**.

AB

- ☒ A. 1 mol Br₂(l) at 1 atm and 8 °C and 1 mol Br₂(s) at 1 atm and -8 °C
☒ B. 10.0 mol of Na(s) at 1 atm and 5 °C and 100.0 g of Na(s) at 1 atm and 5 °C
☒ C. MgS at 1 atm and 25 °C and KBr at 1 atm and 25 °C
☒ D. 0.284 mol O₂ at 15.0 bar and 22.3 °C and 0.312 mol SO₂ at 0.110 bar and 32.5 °C

A: the entropy of the liquid is higher than the solid + entropy increases with temperature

B: Entropy is an extensive property ∴ 10.0 mol of Na(s) has higher entropy than 100.0 g (≈ 4.4 mol) of Na(s)

C: the greater the charges ∴ higher lattice energy & lower entropy

D: SO₂ is heavier & more complex than O₂, more # of modes, lower pressure & higher temperature

6. Which of the following statements is true?

C

- ☒ A. A reaction in which the entropy of the system increases can be spontaneous only if it is exothermic
☒ B. A reaction in which the entropy of the system increases can be spontaneous only if it is endothermic
☒ C. A reaction in which the entropy of the system decreases can be spontaneous only if it is exothermic
☒ D. A reaction in which the entropy of the system decreases can be spontaneous only if it is endothermic
☒ E. None of the above statements are true

A: Entropy of the system can increase, if a reaction is endothermic as well but only at high temperatures

B: Entropy of the system can increase & the reaction is spontaneous if a reaction is endothermic

C: if $\Delta S < 0$ (negative value) ∴ the term $T\Delta S$ is positive & for a reaction to be spontaneous, it has to be exothermic & of a larger magnitude than $T\Delta S$

D: A reaction in which entropy of the system decreases & is endothermic is non-spontaneous at all temperatures

7. Which of the following statement(s) is/are true regarding the combustion of propane (C₃H₈) gas? Select all that apply. Insert letters without spaces in the answer box, example **ABCD**.

AE

- ☒ A. $\Delta H < 0$ and $\Delta S > 0$ for the combustion of propane
☒ B. $\Delta H > 0$ and $\Delta S < 0$ for the combustion of propane
☒ C. The combustion of propane is spontaneous only at low temperatures
☒ D. The combustion of propane is spontaneous only at high temperatures
☒ E. The combustion of propane is spontaneous at all temperatures
☒ F. The combustion of propane is non-spontaneous at any temperatures



* All combustion reactions are exothermic ∴ $\Delta H < 0$

* From the equation, entropy of the system increases (one additional mole of gas produced) ∴ $\Delta S > 0$

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

(-) (+)

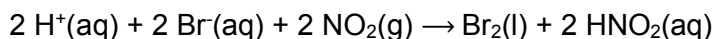
∴ $\Delta G < 0$

the combustion of propane is spontaneous at all temperatures

8. You are given the redox reaction below in acidic medium at 25 °C. $\Delta H_{\text{rxn}} = -61.6 \text{ kJ/mol}$, $\Delta G_{\text{rxn}} = 4.4 \text{ kJ/mol}$, and the standard molar entropies for the reactants and products are also provided below. Calculate the standard molar entropy for HNO_2 in $\text{J/mol}\cdot\text{K}$. Keep your answer to 4 sig figs.

135.7

$\text{J/mol}\cdot\text{K}$



Substance	$\text{H}^+(\text{aq})$	$\text{Br}^-(\text{aq})$	$\text{NO}_2(\text{g})$	$\text{Br}_2(\text{l})$	$\text{HNO}_2(\text{aq})$
$S^\circ (\text{J/mol}\cdot\text{K})$	0	82.4	240.1	152.2	?

step 1:

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

$$4.4 \frac{\text{kJ}}{\text{mol}} = -61.6 \frac{\text{kJ}}{\text{mol}} - (25 + 273.15) \Delta S$$

$$66.0 \frac{\text{kJ}}{\text{mol}} = -298 \text{ K} \times \Delta S$$

$$\therefore \Delta S = \frac{66.0 \frac{\text{kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{1 \text{ kJ}}}{-298 \text{ K}} = -221.47 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

step 2:

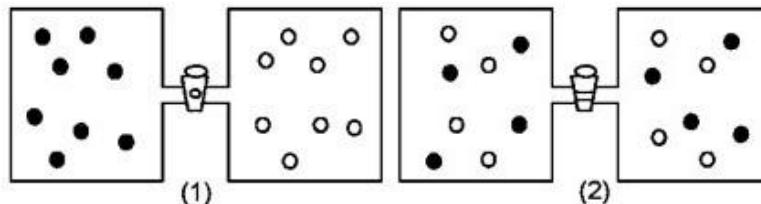
$$\Delta S_{\text{rxn}} = (\sum n_p \times \Delta S^\circ_{\text{products}}) - (\sum n_r \times \Delta S^\circ_{\text{reactants}})$$

$$-221.47651 = [(2 \times x) + (1 \times 152.2)] - [(2 \times 0) + (2 \times 82.4) + (2 \times 240.1)]$$

$$423.5234899 = 2x + 152.2$$

$$x = 135.7 \frac{\text{J}}{\text{mol}\cdot\text{K}}$$

9. In figure (1) below argon atoms, represented by unshaded spheres, and neon atoms, represented by shaded spheres, are in separate compartments in a closed system. Figure (2) shows the equilibrium state of the system after the stopcock separating the two compartments is opened. Assuming that argon and neon behave as ideal gases, what are the signs (+, -, or 0) of ΔH , ΔS , and ΔG for this process?

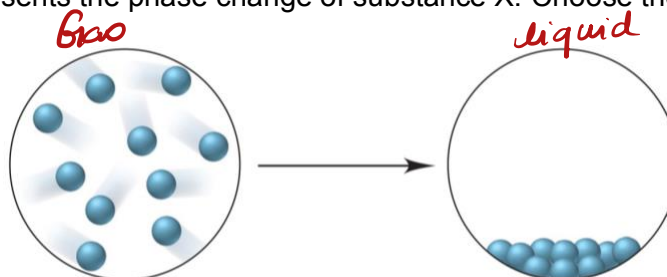


B

- A. $\Delta H = +$, $\Delta S = -$, $\Delta G = +$
 B. $\Delta H = 0$, $\Delta S = +$, $\Delta G = -$
 C. $\Delta H = 0$, $\Delta S = -$, $\Delta G = +$
 D. $\Delta H = -$, $\Delta S = +$, $\Delta G = -$

*NO heat is produced or removed
 the two gases spontaneously mix $\therefore \Delta S > 0$
 if $\Delta G = \Delta H - T\Delta S$
 $\Delta G = 0 - T\Delta S$
 $\therefore \Delta G < 0$*

10. The illustration below represents the phase change of substance X. Choose the correct answer below.

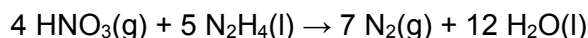


The sign for ΔH for this process is **-** (+ or -) and the sign for ΔS is **-** (+ or -).

This process is **spontaneous** (spontaneous or non-spontaneous) at **low temperatures** (at no temperatures, all temperatures, low temperatures, or high temperatures).

11. You get an internship at NASA, and you learn that the reaction of hydrazine (N_2H_4) and nitric acid is used as rocket propellant. Calculate ΔG_{rxn} in kJ/mol at 25 °C for the reaction of hydrazine and nitric acid using the information provided below. Keep your answer to 3 sig figs and use scientific notation.

$$\boxed{-3.30} \times 10^{\boxed{3}} \text{ kJ/mol}$$



	$\text{HNO}_3(\text{g})$	$\text{N}_2\text{H}_4(\text{l})$	$\text{N}_2(\text{g})$	$\text{H}_2\text{O}(\text{l})$
ΔH° (kJ/mol)	-133.9	50.6	0	-285.8
ΔS° (J/mol·K)	266.9	121.2	191.6	70.0

$$\begin{aligned} \Delta H_{\text{rxn}} &= (\sum n_p \times \Delta H^\circ_{\text{products}}) - (\sum n_r \times \Delta H^\circ_{\text{reactants}}) \\ &= [(7 \times 0) + (12 \times -285.8)] - [(4 \times -133.9) + (5 \times 50.6)] \\ &= (-3429.6) - (-282.6) \\ &= -3147.0 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

$$\begin{aligned} \Delta S_{\text{rxn}} &= (\sum n_p \times \Delta S^\circ_{\text{products}}) - (\sum n_r \times \Delta S^\circ_{\text{reactants}}) \\ &= [(7 \times 191.6) + (12 \times 70.0)] - [(4 \times 266.9) + (5 \times 121.2)] \\ &= 2181.2 - (1673.6) \\ &= 507.6 \text{ J/mol}\cdot\text{K} \end{aligned}$$

$$\begin{aligned} \Delta G_{\text{rxn}} &= \Delta H_{\text{rxn}} - T \Delta S_{\text{rxn}} \\ &= (-3147.0 \frac{\text{kJ}}{\text{mol}} \times \frac{1000 \text{ J}}{1 \text{ kJ}}) - (25 + 273.15 \text{ K}) (507.6 \text{ J/mol}\cdot\text{K}) \\ &= -3.298 \times 10^6 \frac{\text{J}}{\text{mol}} = -3.30 \times 10^6 \frac{\text{J}}{\text{mol}} = -3.30 \times 10^3 \frac{\text{kJ}}{\text{mol}} \end{aligned}$$

12. Which of the following has the highest standard molar entropy?

- A**
- (A) $\text{N}_2\text{F}_4(\text{g})$
 - B. $\text{N}_2\text{H}_4(\text{g})$
 - C. $\text{NO}(\text{g})$
 - D. $\text{NH}_4\text{CO}_2\text{NH}_2(\text{s})$
 - E. $\text{NH}_4\text{OH}(\text{aq})$

$\text{N}_2\text{F}_4(\text{g}) > \text{N}_2\text{H}_4(\text{g}) > \text{NO}(\text{g})$
 greater complexity than NO
 but N_2F_4 is heavier than N_2H_4

Entropy of gas > liquid > solid

13. Which of the following statements is **true** regarding the **second law** of thermodynamics? Select all that apply. Insert letters without spaces in the answer box, example **ABCD**.

AB

- ☒ A. $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$ for any spontaneous process
☒ B. $\Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$ for a reversible process
☒ C. The entropy of a perfect crystal at absolute zero (0 K) is zero
☒ D. The energy of the universe is conserved in any process
☒ E. All the above of the statements are true

A. $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$ irreversible or spontaneous
 $\therefore \Delta S_{\text{sys}} > -\Delta S_{\text{surr}}$
B. $\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$ reversible or equilibrium
 $\therefore \Delta S_{\text{sys}} = -\Delta S_{\text{surr}}$
C. third law of thermodynamics
D. First law of thermodynamics $\Delta E_{\text{univ}} = \Delta E_{\text{sys}} + \Delta E_{\text{surr}}$
 $\Delta E_{\text{sys}} = -\Delta E_{\text{surr}}$

14. Which of the following processes are spontaneous or non-spontaneous? Insert (S) for spontaneous and (NS) for non-spontaneous.

NS

A. Splitting of water into hydrogen gas and oxygen gas

S

B. Dissolving table salt (NaCl) in water

S

C. Ripening of a banana

S

D. Vaporization of $\text{Br}_2(\text{l})$ at 60.0°C (boiling point of $\text{Br}_2(\text{l}) = 58.8^\circ\text{C}$)

S

E. Combustion of natural gas (natural gas is a mixture of methane and ethane)

NS

F. Driving a car up the hill