

## 2<sup>nd</sup> Law of Thermodynamics – Supplemental Worksheet

1. Consider the 2<sup>nd</sup> law of thermodynamics explain what the signs of  $\Delta S_{\text{universe}}$ .

- a)  $\Delta S_{\text{universe}} \geq 0$  *The entropy of the universe will increase and the process is spontaneous in the direction as written.*
- b)  $\Delta S_{\text{universe}} \leq 0$  *The entropy of the universe will decrease and the process is spontaneous in the opposite direction.*
- c)  $\Delta S_{\text{universe}} = 0$  *The system is at equilibrium and will not occur.*

2. If a system at  $-272\text{ }^{\circ}\text{C}$  absorbs 545 J of heat, what is its change in entropy?

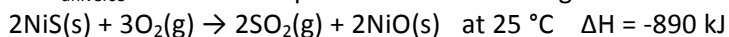
$$\Delta S = q/T = 545/1 = 545 \text{ J}\cdot\text{K}^{-1}$$

3. Consider the following reaction:  $\text{HNO}_3(\text{l}) + 1/2\text{H}_2(\text{g}) \leftrightarrow \text{H}_2\text{O}(\text{l}) + \text{NO}_2(\text{g})$  Calculate  $\Delta S^{\circ}_{\text{rxn}}$

	$\Delta H^{\circ}_f$ (kJ·mol <sup>-1</sup> )	$\Delta S^{\circ}_m$ (J·mol <sup>-1</sup> ·K <sup>-1</sup> )
HNO <sub>3</sub> (l)	-174.1	156
H <sub>2</sub> (g)	not provided	131
H <sub>2</sub> O(l)	-285.8	70
NO <sub>2</sub> (g)	33.2	240

$$\begin{aligned} \Delta S_{\text{rxn}} &= \sum S_{m,\text{products}} - \sum S_{m,\text{reactants}} \\ &= (70 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} + 240 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) - (156 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} + (0.5)131 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \\ &= 88.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 0.0885 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \end{aligned}$$

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



<u>Substance</u>	<u>S(J/Kmole)</u>
SO <sub>2</sub>	248
NiO	38
O <sub>2</sub>	205
NiS	53

$$\begin{aligned} \Delta S_{\text{sys}} &= [2(248) + 2(38)] - [2(53) + 3(205)] = -149 \text{ J/K} \\ \Delta S_{\text{surr}} &= -\Delta H/T = -(-890 \text{ kJ})/298 \text{ K} = 3.0 \text{ kJ/K} \\ \Delta S_{\text{universe}} &= \Delta S_{\text{sys}} + \Delta S_{\text{surr}} = -149 \text{ J/K} + 3000 \text{ J/K} = 2851 \text{ J/K} \end{aligned}$$

5. Determine the  $\Delta S_{\text{sys}}$  when:

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

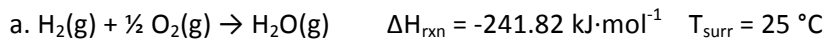
$$\Delta H = -387.4 \text{ kJ}$$

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

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

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

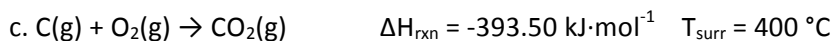
6. Calculate  $\Delta S_{\text{surroundings}}$  for the reactions below based on the provided data.



$$\Delta S_{\text{surr}} = -\Delta H_{\text{rxn}}/T_{\text{surr}} = 241.82 \text{ kJ}\cdot\text{mol}^{-1}/298 \text{ K} = 0.811 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$



$$\Delta S_{\text{surr}} = -\Delta H_{\text{rxn}}/T_{\text{surr}} = -90.00 \text{ kJ}\cdot\text{mol}^{-1}/193 \text{ K} = -0.466 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$



$$\Delta S_{\text{surr}} = -\Delta H_{\text{rxn}}/T_{\text{surr}} = 393.50 \text{ kJ}\cdot\text{mol}^{-1}/673 \text{ K} = 0.584 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

7. A certain reaction (the system) is endothermic by  $45.68 \text{ kJ}\cdot\text{mol}^{-1}$  and its entropy increases by  $172.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ . Calculate  $\Delta S_{\text{universe}}$ , if the surroundings are at a constant temperature of  $0 \text{ }^\circ\text{C}$ . Can the reaction occur at this temperature? If not, should we raise or lower the temperature to make it spontaneous.

$$\Delta S_{\text{univ}} = \Delta S_{\text{surr}} + \Delta S_{\text{sys}} = -\Delta H_{\text{rxn}}/T_{\text{surr}} + \Delta S_{\text{sys}}$$

$$\Delta S_{\text{univ}} = -45,680 \text{ kJ}\cdot\text{mol}^{-1} / 273 \text{ K} + 172.3 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 4.97 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

Yes, this reaction can occur at this temperature because  $\Delta S_{\text{univ}}$  is positive which indicates the reaction is spontaneous.

8. Calculate the change in entropy that occurs when a 3.50 mol sample of water is heated from  $65^\circ$  to  $130^\circ$  at 1 atm. The molar heat capacities for  $\text{H}_2\text{O}(\text{l})$  is  $75.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  and  $\text{H}_2\text{O}(\text{g})$  is  $36.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . The enthalpy of vaporization for water is  $40.7 \text{ kJ/mol}$  at  $100^\circ\text{C}$ .

*In this problem, you are asked for the change in the sample which is a total of 3.50 moles of water. Therefore you must take into account the number of moles in the equation, n. If the question ask for per mole, then you do not need to take into account the number of moles.*

1.  $\Delta S(\text{l})$  heating liquid  $65^\circ \rightarrow 100^\circ\text{C}$

$$\Delta S = n C \ln(T_f/T_i) = (3.50 \text{ mol})(75.3 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) \ln(373/338) = 26.0 \text{ J}\cdot\text{K}^{-1}$$

2.  $\Delta S$  liquid to gas at  $100^\circ\text{C}$

$$\Delta S = \Delta H_{\text{vap}}/T_{\text{bp}} = 40.7 \text{ kJ}\cdot\text{mol}^{-1} / 373 \text{ K} = 0.109 \text{ kJ}\cdot\text{K}^{-1}\cdot\text{mol}^{-1} = 109 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

*This is for 1 mol, therefore you must take into account 3.50 moles.*

$$\Delta S = (109 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(3.50 \text{ mol}) = 382 \text{ J}\cdot\text{K}^{-1}$$

3.  $\Delta S(\text{g})$  heating gas  $100^\circ \rightarrow 130^\circ\text{C}$

$$\Delta S = n C \ln(T_f/T_i) = (3.50 \text{ mol})(36.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}) \ln(403/373) = 9.86 \text{ J}\cdot\text{K}^{-1}$$

$$\Delta S_{\text{Total}} = 26.0 \text{ J}\cdot\text{K}^{-1} + 382 \text{ J}\cdot\text{K}^{-1} + 9.86 \text{ J}\cdot\text{K}^{-1} = 417 \text{ J}\cdot\text{K}^{-1}$$