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2nd Law of Thermodynamics – Supplemental Worksheet

1. Consider the 2nd law of thermodynamics explain what the signs of $\Delta S_{universe}$.

   a) $\Delta S_{universe} \geq 0$ *The entropy of the universe will increase and the process is spontaneous in the direction as written.*

   b) $\Delta S_{universe} \leq 0$ *The entropy of the universe will decrease and the process is spontaneous in the opposite direction.*

   c) $\Delta S_{universe} = 0$ *The system is at equilibrium and will not occur.*

2. If a system at -272 °C absorbs 545 J of heat, what is its change in entropy?

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

3. Consider the following reaction: $HNO_3(l) + 1/2H_2(g) \leftrightarrow H_2O(l) + NO_2(g)$ Calculate $\Delta S°_{rxn}$

	$\Delta H°_f$ ($kJ \cdot mol^{-1}$)	$\Delta S°_m$ ($J \cdot mol^{-1} \cdot K^{-1}$)
$HNO_3(l)$	-174.1	156
$H_2(g)$	not provided	131
$H_2O(l)$	-285.8	70
$NO_2(g)$	33.2	240

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

4. Calculate $\Delta S_{universe}$ after the completion of the following reaction:
   $2NiS(s) + 3O_2(g) \rightarrow 2SO_2(g) + 2NiO(s)$ at 25 °C $\Delta H = -890$ kJ

Substance	S(J/Kmole)
SO_2	248
NiO	38
O_2	205
NiS	53

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

5. Determine the ΔS_{sys} when:

$\Delta S_{universe}$ = 1303 J/K
ΔH = -387.4 kJ
T = 25 °C

$\Delta H = -T\Delta S_{surr} \rightarrow \Delta S_{surr} = -\Delta H/T = -(-387.4\ kJ)/298K = 1.3\ kJ/K$
$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \rightarrow \Delta S_{sys} = \Delta S_{univ} - \Delta S_{surr} = 1303\ J/K - 1300\ J/K = 3\ J/K$

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

a. $H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow H_2O(g)$ $\Delta H_{rxn} = -241.82\ kJ\cdot mol^{-1}$ T_{surr} = 25 °C
$\Delta S_{surr} = -\Delta H_{rxn}/T_{surr} = 241.82\ kJ\cdot mol^{-1}/298\ K = 0.811\ kJ\cdot mol^{-1}\cdot K^{-1}$

b. $\frac{1}{2}\ N_2(g) + \frac{1}{2}\ O_2(g) \rightarrow NO(g)$ $\Delta H_{rxn} = 90.00\ kJ\cdot mol^{-1}$ T_{surr} = -80 °C
$\Delta S_{surr} = -\Delta H_{rxn}/T_{surr} = -90.00\ kJ\cdot mol^{-1}/193\ K = -0.466\ kJ\cdot mol^{-1}\cdot K^{-1}$

c. $C(g) + O_2(g) \rightarrow CO_2(g)$ $\Delta H_{rxn} = -393.50\ kJ\cdot mol^{-1}$ T_{surr} = 400 °C
$\Delta S_{surr} = -\Delta H_{rxn}/T_{surr} = 393.50\ kJ\cdot mol^{-1}/673\ K = 0.584\ kJ\cdot mol^{-1}\cdot K^{-1}$

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

$\Delta S_{univ} = \Delta S_{surr} + \Delta S_{sys} = -\Delta H_{rxn}/T_{surr} + \Delta S_{sys}$
$\Delta S_{univ} = -45{,}680\ kJ\cdot mol^{-1}/273\ K + 172.3\ J\cdot mol^{-1}\cdot K^{-1} = 4.97\ J\cdot mol^{-1}\cdot K^{-1}$
Yes, this reaction can occur at this temperature because ΔS_{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° to 130° at 1 atm. The molar heat capacities for H_2O (l) is 75.3 $JK^{-1}mol^{-1}$ and H_2O (g) is 36.4 $JK^{-1}mol^{-1}$. The enthalpy of vaporization for water is 40.7 kJ/mol at 100°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. ΔS (l) heating liquid 65° → 100°C
$\Delta S = n\ C\ ln\ (T_f/T_i) = (3.50\ mol)(75.3\ JK^{-1}mol^{-1})\ ln\ (373/338) = 26.0\ JK^{-1}$

2. ΔS liquid to gas at 100°C
$\Delta S = \Delta H_{vap}/T_{bp} = 40.7\ kJmol^{-1}/373\ K = 0.109\ kJK^{-1}mol^{-1} = 109\ JK^{-1}mol^{-1}$
This is for 1 mol, therefore you must take into account 3.50moles.
$\Delta S = (109\ JK^{-1}mol^{-1})(3.50mol) = 382\ JK^{-1}$

3. ΔS (g) heating gas 100° → 130°C
$\Delta S = n\ C\ ln\ (T_f/T_i) = (3.50\ mol)(36.4\ JK^{-1}mol^{-1})\ ln\ (403/373) = 9.86\ JK^{-1}$

$\Delta S_{Total} = 26.0\ JK^{-1} + 382\ JK^{-1} + 9.86\ JK^{-1} = 417\ JK^{-1}$