

Handout 11 selected Answers:

3. Consider 4 “X” particles and 3 quanta of energy in 5 boxes (shown below). If one of the particles and one quantum of energy removed, calculate the change in entropy in J/K to one significant figure. Is this process spontaneous?

X	X	
X	X	

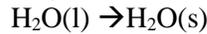
$$W_{\text{sys(initial)}} = W_p \cdot W_q = 5 \cdot 20 = 100$$

$$W_{\text{sys(final)}} = W_p \cdot W_q = 10 \cdot 6 = 60$$

$$\Delta S_{\text{system}} = k_B 2.3 \log \frac{W_{\text{final}}}{W_{\text{initial}}} = 1.38 \cdot 10^{-23} \text{ J/K} \cdot 2.3 \cdot \log 0.6 = -0.7 \cdot 10^{-23} \text{ J/K} \quad \text{Not}$$

spontaneous

5. At -1 °C, liquid water spontaneously freezes.



- For this process, the entropy change of the system, ΔS_{sys} is: $\Delta S_{\text{sys}} < \mathbf{0}$
- During the process of freezing, are H-bond broken or formed? Formed
- During the process of freezing ΔH_{sys} is: $\Delta H_{\text{sys}} < \mathbf{0}$
- During the process of freezing ΔH_{sur} is: $\Delta H_{\text{sur}} \geq \mathbf{0}$
- At -1 °C, liquid water spontaneously freezes. For this process, the entropy change of the surroundings, ΔS_{surr} is: $\Delta S_{\text{surr}} \geq \mathbf{0}$
- At -1 °C, liquid water spontaneously freezes. For this process, in comparison to the *magnitude* of the entropy change of the system, the *magnitude* of the entropy change of the surroundings $|\Delta S_{\text{sur}}|$, is ...
- At -1°C ΔS_{univ} of the process will be: $\Delta S_{\text{univ}} \geq \mathbf{0}$
- At +1°C ΔS_{univ} of the process will be: $\Delta S_{\text{univ}} < \mathbf{0}$
- At 0°C ΔS_{univ} of the process will be: $\Delta S_{\text{univ}} = \mathbf{0}$
- (At home) If $\Delta H_{\text{fus(water)}} = 6.00 \text{ kJ/mol}$ calculate ΔS_{sys} , ΔS_{sur} and ΔS_{univ} at -1°C and at 1°C.

$$\Delta H_{\text{fus(water)}} = 6.00 \text{ kJ/mol for } \text{H}_2\text{O(s)} \rightarrow \text{H}_2\text{O(l)}$$

$$\Delta H(\text{l} \rightarrow \text{s}) = -\Delta H_{\text{fus}} = -6.00 \text{ kJ/mol}$$

$$\text{At } \mathbf{-1^\circ\text{C}} \quad \Delta S_{\text{sys}} = \Delta S_{\text{rxn}} = \frac{\Delta H_{\text{sys}}}{T_{\text{eq}}} = \frac{-6.00 \text{ kJ/mol}}{273.15 \text{ K}} = -21.97 \frac{\text{J}}{\text{molK}}$$

$$\Delta S_{\text{sur}} = -\frac{\Delta H_{\text{sys}}}{T} = -\frac{-6.00 \text{ kJ/mol}}{272.15 \text{ K}} = 22.05 \frac{\text{J}}{\text{molK}}$$

$$\Delta S_{\text{univ}} = \Delta S_{\text{net}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} = (22.05 - 21.97) \frac{\text{J}}{\text{molK}} = 0.08067 \frac{\text{J}}{\text{molK}}$$

13. I like making “sweet tea” and thought making ice cubes of sugar water would be useful. However, when I put my sugar water in my freezer at 0°C, the sugar water did not freeze. **Circle the correct statements** and **correct any incorrect statements** for the freezing of sugar water. (HINT: You might use the diagram above to assist you.)

- Explonatin:
 $\Delta H_{\text{melt,soln}} = \Delta H_{\text{melt,water}}$
- a. $\Delta H_{\text{melt,soln}} > \Delta H_{\text{melt,water}}$
- b. $\Delta S_{\text{freeze,soln}} < \Delta S_{\text{freeze,water}}$**
- c. $\Delta S_{\text{freeze,soln}} > \Delta S_{\text{freeze,water}}$ $\Delta S_{\text{freeze,soln}} < \Delta S_{\text{freeze,water}}$
- d. $|\Delta S_{\text{freeze,soln}}| > |\Delta S_{\text{freeze,water}}|$**
- e. $|\Delta S_{\text{freeze,soln}}| < |\Delta S_{\text{freeze,water}}|$ $|\Delta S_{\text{freeze,soln}}| > |\Delta S_{\text{freeze,water}}|$
- f. $S_{\text{liquid,water}} > S_{\text{soln}}$ $S_{\text{liquid,water}} < S_{\text{soln}}$
- g. $\Delta H_{\text{melt,soln}}$ **is NOT** temperature dependent

18. Consider the process of adding 1 quantum of energy to a system:

System A: $W_{\text{initial}}(4_{\text{atoms}}, 10_{\text{quanta}}) \rightarrow W_{\text{final}}(4_{\text{atoms}}, 11_{\text{quanta}})$

System B: $W_{\text{initial}}(4_{\text{atoms}}, 4_{\text{quanta}}) \rightarrow W_{\text{final}}(4_{\text{atoms}}, 5_{\text{quanta}})$

Which process has the greater entropy change (ΔS): **B**

Prove your answer (by comparing the number of arrangements):

$$\text{System A} \rightarrow \left(\frac{W_{\text{final}}}{W_{\text{initial}}}\right)_A = \frac{q+m}{q+1} = \frac{(11+4-1)!}{10!(4-1)!} = \frac{14!}{10!3!} = \frac{14! \cdot 10! \cdot 3!}{13! \cdot 11! \cdot 3!} = \frac{14}{11} = 1.27$$

$$\text{System B} \rightarrow \left(\frac{W_{\text{final}}}{W_{\text{initial}}}\right)_B = \frac{(5+4-1)!}{4!(4-1)!} = \frac{8!}{4!3!} = \frac{8! \cdot 4! \cdot 3!}{7! \cdot 5! \cdot 3!} = \frac{8}{5} = 1.6$$

ΔS_a verses ΔS_b the same as comparing $\left(\frac{W_{\text{final}}}{W_{\text{initial}}}\right)_a$ verses $\left(\frac{W_{\text{final}}}{W_{\text{initial}}}\right)_b$

$$1.6 > 1.3 \rightarrow \Delta S_{\text{system B}} > \Delta S_{\text{system A}}$$

2. Fill the table by using the following possible answers (T_{eq} is the temperature at equilibrium):

ΔH_{sys}	ΔS_{sys}	ΔS_{net} (specify at which temperature)
Exothermic	Positive	Always spontaneous process
Exothermic	Negative	Only spontaneous at $T < T_{\text{eq}}$
Endothermic	Positive	Only spontaneous $T > T_{\text{eq}}$
Endothermic	Negative	Never spontaneous

