WORKSHEET: ENTROPY - SOLUTIONS

Entropy Changes

1. Entropy is a thermodynamic function that measures randomness or disorder.

2. Spontaneity refers to a process that happens without any outside intervention. It does not say anything about how fast a reaction will occur.

3. The second law of thermodynamics states that in any spontaneous process the entropy of the universe increases.

4. For some of these reactions the sign of $\Delta S$ can be estimated easily. Others require more careful consideration or even calculation.

a) The volume in this reaction increases greatly, because 1 mole of gas is formed. This makes the products more disordered than the reactants. Therefore, the $\Delta S$ is (+).

b) The volume in this reaction decreases greatly because the number of moles of gas decreases from 3 to 0. This $\Delta S$ is (-).

c) Although it is harder to guess the sign of $\Delta S$, because there is no significant volume change, one would assume that $\Delta S$ increases, because the NaCl dissociates into ions the products are more disordered than the reactants. To be sure one could calculate $\Delta S$ using the values in the syllabus appendix

$$\Delta S = [(55.2 \text{ J/mol}\cdot\text{K}) + (60.2 \text{ J/mol}\cdot\text{K}) + (69.94 \text{ J/mol}\cdot\text{K})] - [(72.4 \text{ J/mol}\cdot\text{K}) + (69.94 \text{ J/mol}\cdot\text{K})]$$

$$= 43 \text{ J/mol}\cdot\text{K}$$

d) Again the volume does not change significantly. The easiest way to tell is to calculate $\Delta S$ using the table in your syllabus.

$$\Delta S = [(222.95 \text{ J/mol}\cdot\text{K}) + (130.59 \text{ J/mol}\cdot\text{K})] - [2(186.68)\cdot\text{K}]$$

$$= -19.82 \text{ J/mol}\cdot\text{K} \quad \text{so } \Delta S \text{ (-)}$$

e) Same as d) - calculate $\Delta S$ to be sure.

$$\Delta S = [2(210.62 \text{ J/mol}\cdot\text{K})] - [(191.49 \text{ J/mol}\cdot\text{K}) + (205.03)]$$

$$= 24.72 \text{ J/mol}\cdot\text{K} \quad \text{so } \Delta S \text{ (+)}$$

f) Increasing the pressure of a gas decreases the volume which means the molecules will be more ordered thus $\Delta S$ is (-).

g) Cooling a gas also decreases the volume of the gas so $\Delta S$ is (-).

h) The volume in this reaction increases greatly, because the number of moles of gas increases. This means $\Delta S$ is (+).

i) Expanding a gas into a vacuum increases the volume occupied by the gas so $\Delta S$ is (+).
Absolute Entropies

5. a) Hg(l), liquid more disorder than solid.
   b) HI, larger molecule, more complex at atomic level
   c) NH₃, more complicated.
   d) C₂H₆, both more complicated and larger.
   e) H₂(g). One mole at one atm has a greater volume than one mole at two atm: more microstates.
   f) NaCl(aq). Mixtures are more disordered.

Entropy Changes for Phase Transitions

6. Warming ice from -273°C (0 K) to 0°C \( \rightarrow \Delta S(+) \) because the molecules begin to move more as T increases.

Ice melting at 0°C \( \rightarrow \Delta S(+) \) because entropy increases as ice melts; phase change from solid to liquid.

Heating of liquid from 0°C to 100°C \( \rightarrow \Delta S(+) \) because the molecules move around more as T increases.

Vaporization of liquid at 100°C \( \rightarrow \Delta S(+) \) because entropy increases as water boils; phase change from liquid to gas.

Heating of gas above 100°C \( \rightarrow \Delta S(+) \) because the molecules move around more as T increases.

The most dramatic changes are at the phase changes from s \( \rightarrow \) l and l \( \rightarrow \) g because the disorder increases much more at these points.

Ice melts spontaneously at temperatures above \( \rightarrow \) 0°C.
Water freezes spontaneously at temperatures below 0°C.
Water boils spontaneously at temperatures above 100°C.
Steam condenses spontaneously at temperatures below 100°C.
7. \( \Delta S_{\text{rev}} = \Delta S_{\text{subt}} + \Delta S \)

for \(-20^\circ\text{C} (253 \text{ K})\)

\[
\Delta S_{\text{subt}} = \frac{-6.03 \times 10^3 \text{ J/mol}}{253 \text{ K}} + 22.1 \text{ J/Kmol} = \underline{1.7 \text{ J/Kmol}}; \text{ melting does not occur spontaneously}
\]

for \(0^\circ\text{C} (273 \text{ K})\)

\[
\Delta S_{\text{subt}} = \frac{-6.03 \times 10^3 \text{ J/mol}}{273 \text{ K}} + 22.1 \text{ J/Kmol} = 0 \text{ J/Kmol}; \text{ equilibrium; melting point}
\]

for \(+20^\circ\text{C} (293 \text{ K})\)

\[
\Delta S_{\text{subt}} = \frac{-6.03 \times 10^3 \text{ J/mol}}{293 \text{ K}} + 22.1 \text{ J/Kmol} = \underline{+1.52 \text{ J/Kmol}}; \text{ melting occurs spontaneously}
\]

Additional problems

8. The third law of thermodynamics states that at 0 K, the entropy of a perfectly crystalline pure substance is zero.

9. \( \Delta S_{\text{rxn}}^\circ = \sum S^\circ (\text{prod}) - \sum S^\circ (\text{react}) \)

\[\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \text{ if } \Delta G^\circ, \Delta H^\circ \text{ and } T \text{ are known} \]

10. The standard units for entropy are J/K•mol. Standard states are 1 molar solutions or gases at 1 atm pressure.

11. \( \Delta S_{\text{rxn}}^\circ = \sum S^\circ (\text{prod}) - \sum S^\circ (\text{react}) \)

\[
= [2(192.5 \text{ J/mol•K})] - [(191.49) + 3(130.59)]
\]

\[= -198.26 \text{ J/mol•K} \]

This number makes sense. One would expect \( \Delta S^\circ \) for this reaction to be negative because the number of moles of gas decreases in going from reactants to products.

12. \( \Delta S_{\text{universe}} = \Delta S_{\text{subt}} + \Delta S_{\text{sys}} \); the second law states that for a spontaneous process \( \Delta S_{\text{universe}} \) is (+).

13. \( q, \Delta E, \Delta H, \Delta S \)

\[ + + + + \]

14. \( \Delta H = + \text{ endothermic} \)

\( \Delta S = + \text{ increase} \)

15. 13