Name ____________________________**Chem 163 Section**: ______ **Team Number:** ______

ALE 20. Calculating ΔS & Predicting Spontaneity of Reaction

(Reference: 20.1 - 20.2 Silberberg 5th *edition*)

Will a non-spontaneous process occur if the temperature is increased?

The Model: Calculating the Change in Entropy for a Reaction

The entropy of a (non-aqueous ion) substance at any temperature above 0 K is positive and is related to the substance's Third Law Entropy (*i.e.*, $S = 0$ at 0 K for a "perfect crystal") through the substance's heat capacity. Since chemists are typically interested in reactions occurring at a temperature of 25 °C, the standard state molar entropies (*i.e.*, $S°$, where the superscript naught informs the reader that a gas exerts a pressure of 1 atm and solids and liquids are under a pressure of 1 atm) of substances are usually tabulated for a temperature of 25 °C.

In Chem 161 we learned that we can use tabulated standard heats of formation (ΔH_f^o) to calculate the heat of a reaction via Hess's Law (eqn **1**)

$$\Delta H^o_{rxn} = \sum_{p} n_p \, \Delta H^o_f(p) - \sum_{r} n_r \, \Delta H^o_f(r) \qquad \textbf{(1)}$$

sum over **p**roducts   sum over **r**eactants

where n_i is the i^{th} species' stoichiometric coefficient in the balanced chemical equation. What makes Hess's Law possible for heats of reaction is that enthalpy is a **state function**.

Key Question

1. Since entropy is a state function, there must be a version of "Hess's Law" for changes of entropy in a system when a chemical reaction occurs. Consider the generic chemical reaction shown as eqn **2**.

$$a\,A + b\,B \rightarrow d\,D + e\,E \qquad \textbf{(2)}$$

Write the formula that would be used to determine the change in entropy for the eqn **2** based on the tabulated values of standard molar entropies of the reactants and products. (Note: Tabulated standard molar entropies are "$S°$" and not "ΔS^o_f".)

Exercises

2. For the following reactions: ① Predict whether the entropy of the system will decrease or increase and briefly explain why; and ② Then use the table of thermodynamic data to determine the standard change in entropy at 25 °C for each of the following reactions and compare the sign of ΔS with what you predicted.

   a. $2\ KClO_3(s) \rightarrow 2\ KCl(s) + 3\ O_2(g)$

      Prediction: Entropy increases   Entropy decreases   (circle your choice)

      Explanation:

      Calculation of ΔS: *(Circle your answer!)*

   b. $NO(g) + SO_3(g) \rightarrow NO_2(g) + SO_2(g)$

      Prediction: Entropy increases   Entropy decreases   (circle your choice)

      Explanation:

      Calculation of ΔS: *(Circle your answer!)*

   c. $2\ NaOH(aq) + FeCl_2(aq) \rightarrow Fe(OH)_2(s) + 2\ NaCl(aq)$ (*Hint*: First write the net ionic equation.)

      Net ionic Equation: ____

      Prediction: Entropy increases   Entropy decreases   (circle your choice)

      Explanation:

      Calculation of ΔS: *(Circle your answer!)*

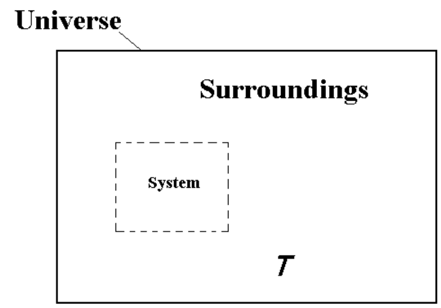
      $S°$ for $Fe(OH)_2(s)$ = **87.93 J mol^{-1} K^{-1}** (source: NIST)

      $S°$ for $Fe^{2+}_{(aq)}$ = **–137.7** J mol^{-1} K^{-1} (from multiple sources; the value for $Fe^{2+}_{(aq)}$ in *Silberberg* is ***incorrect***!)

The Model: Predicting the Spontaneity of a Reaction

The "system" is simply the chemical reactants and products under investigation. The "surroundings" is everything else, and the system and the surroundings together comprise the "universe" (*i.e.*, an isolated system unto itself). What separates the system from the surroundings is perhaps some barrier (*e.g.*, a beaker in which the system is undergoing a chemical reaction), which is classified based on whether matter, heat energy, and/or work energy can pass from one side to the other freely.

We can represent the system and its surrounding by a simple diagram. In the diagram, the temperature of the surroundings is represented by *T*. Since the surroundings are so large (It's the rest of a universe compared to the small system under investigation!), it is convenient to think of the surroundings as a "infinite thermal reservoir". Small amounts of heat deposited into or withdrawn from the surroundings won't significantly affect the temperature of the surroundings.

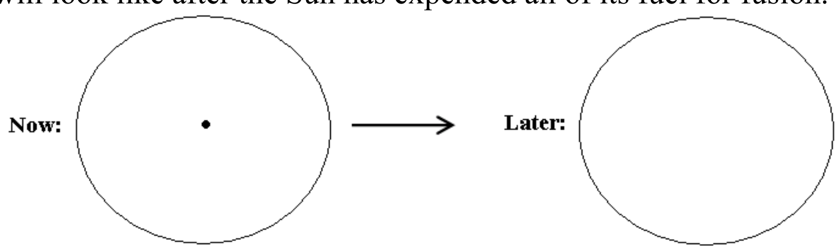


Key Questions

3. A **nonspontaneous process** requires a continuous input of energy from an outside source in order to occur (e.g. photosynthesis requires light energy to occur.) On the other hand, a **spontaneous process** occurs without any outside assistance in the form of energy (occurs naturally). When I think of a process occurring spontaneously, all I need to do is consider the Sun. Compared to the rest of the Universe, it is a concentrated mass of mostly hydrogen (about1.8 × 10^{39} kg worth). In the Sun's core the temperature is ~1.5 × 10^{7} K, and at its surface the temperature is ~6 × 10^{3} K. The temperature of the vacuum of space is 2.7 K. Nuclear fusion takes place within the Sun, the primary process being Hydrogen-1 fusing to become Helium-4. By-products of this nuclear reaction are heat and photons.

    a. Are the processes occurring within the Sun endothermic or exothermic? (Circle your choice.)

    b. While certainly the Sun isn't very large compared to the rest of the Universe, in the figure below the sun's concentrated energy (the combined mass and electromagnetic) is represented by "•" and the surrounding circle the current extent of the Universe. In the circle to the right, sketch what the "later" picture will look like after the Sun has expended all of its fuel for fusion.



    c. Is the "now" or the "later" picture of the Sun's energy more disordered? *Briefly explain your answer*.

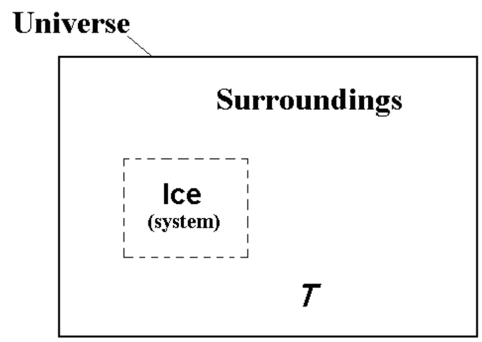
4. Nature prefers processes in which: (Circle the correct answer.)
    i. heat is released from the system into the surroundings; and entropy of the system increases.
    ii. heat is released from the system into the surroundings; and entropy of the system decreases.
    iii. heat is absorbed by the system from the surroundings; and entropy of the system increases.
    iv. heat is absorbed by the system from the surroundings; and entropy of the system decreases.

5. If a proposed reaction is exothermic and the entropy of the chemical system increases, the reaction:
   i. will always be non-spontaneous, but can occur if work is done on the system.
   ii. can be spontaneous, but it will depend on the temperature at which the reaction is taking place.
   iii. will always be spontaneous, but it doesn't necessarily occur instantaneously.

6. If a proposed reaction is endothermic and the entropy of the chemical system decreases, the reaction:
   i. will always be non-spontaneous, but can occur if work is done on the system.
   ii. can be spontaneous, but it will depend on the temperature at which the reaction is taking place.
   iii. will always be spontaneous and occurs instantaneously.

7. There are numerous examples of endothermic processes in which the entropy of the system increases. An everyday example is the melting of ice: **$H_2O(s) \rightarrow H_2O(l)$**

   The diagram to the right represents ice in a room, the temperature of which is above 0 °C.



   a. Explain why the entropy of the system is increasing.

   b. Heat flows from cold to hot / hot to cold. (Circle the correct answer.)
   c. Draw an arrow, labeled with "*q*", in the above diagram that describes the direction in which heat flows between the ice and its surroundings.
   d. What kind of temperature must the surroundings have relative to the ice so that heat will flow in the direction that is the answer to part (c): low or high? (Circle your answer.)

8. There are numerous examples of exothermic processes in which the entropy of the system decreases. Think about everyday processes that you are familiar with that fall in this category. Describe it below and draw a diagram that shows the system in its universe. Indicate how heat must flow between the system and its surrounding by drawing an arrow labeled with "*q*". Determine whether the process occurs at "low" or "high" temperatures.

Exercises

For each of the following thermochemical equations, predict whether the reaction has a $\Delta S° < 0$ or $\Delta S° > 0$. (Do not calculate this quantity using the table of thermodynamic data in your textbook.) Then if the reaction will be: (I) spontaneous at all temperatures; (II) spontaneous at low temperatures (but non-spontaneous at high temperatures); (III) spontaneous at high temperatures (but non-spontaneous at low temperatures); or (IV) non-spontaneous at any temperature. *Briefly explain your reasoning in each*.

9. $2\ HgO(s) \rightarrow 2\ Hg(l) + O_2(g)$ $\Delta H° = 90.8$ kJ

$\Delta S°$ ______ 0 Spontaneous at ________________________________

Reasoning:

10. $4\ Fe(s) + 3\ O_2(g) \rightarrow 2\ Fe_2O_3(s)$ $\Delta H° = -1648.4$ kJ

$\Delta S°$ ______ 0 Spontaneous at ________________________________

Reasoning:

11. $N_2(g) + 3\ Cl_2(g) \rightarrow 2\ NCl_3(g)$ $\Delta H° = 460$ kJ

$\Delta S°$ ______ 0 Spontaneous at ________________________________

Reasoning:

12. $2\ NH_4NO_3(s) \rightarrow 2\ N_2(g) + 4\ H_2O(g) + O_2(g)$ $\Delta H° = -225.5$ kJ

$\Delta S°$ ______ 0 Spontaneous at ________________________________

Reasoning:

13. Distinguish between the terms ***spontaneous*** and ***instantaneous***. Give an example of a process that is spontaneous but very slow, and one that is fast but not spontaneous.

14. Distinguish between the terms ***spontaneous*** and ***nonspontaneous***. Can a nonspontaneous process occur? *Explain*.

15. Why is the ΔS_{vap} of a substance always larger than ΔS_{fus}?

16. Without doing a calculation, predict if ΔS_{sys} for each process is greater than or less than zero. Be *able* to defend your responses.

    a.) Gasoline vapors mixing with air in a car engine: $\Delta S°$ ______ 0

    b.) Hot air expanding: $\Delta S°$ ______ 0

    c.) Breath condensing in cold air: $\Delta S°$ ______ 0

17. Without doing a calculation predict compound of each pair has the greater molar entropy. Be *able* to defend your responses. (Circle your response.)

    a.) $NO_{2\,(g)}$ or $N_2O_{4\,(g)}$ b.) $CH_3OCH_{3(l)}$ or $CH_3CH_2OH_{(l)}$ (*Hint*: consider their IMF's.) c.) $HCl_{\,(g)}$ or $HBr_{(g)}$

18. Without consulting Appendix B, arrange each of the following groups in order of *decreasing* standard molar entropy, S^0. Be *able* to defend your responses.

    a.) The following three metals: Mg, Ca, Ba: ____________________

    b.) Hexane (C_6H_{14}), benzene (C_6H_6), cyclohexane (C_6H_{12}) ____________________

    c.) $PF_2Cl_{3\,(g)}$, $PF_{5\,(g)}$, $PF_{3\,(g)}$ ____________________