

CH302 Worksheet 13c Answer Key—Problems related to lecture on entropy

Listed below are a collection of problems lifted from the entropy chapter in the text book. Although you have already seen some of the entropy material, specifically Worksheet 11 material that includes Hess' law-like calculations of ΔS_{rxn} and assigning the sign of entropy for a physical process based on changes in complexity, and Chapter 13a material on statistical thermodynamics, in this worksheet I provide a collection of entropy calculations in sequence that tie together the majors themes of this profoundly important concept.

1. First the simple definition of the change in entropy based on the amount of heat involved at a constant temperature Calculate the change in entropy of a large block of ice when 50. J of energy is removed reversibly from it as heat at 0°C in a freezer.

Answer: $-0.18 \text{ J}\cdot\text{K}^{-1}$

2. Now, given that the definition of the change in entropy corresponds nicely to a phase change, you can use the same equation (with ΔH representing the amount of heat to prompt every molecule in the system to undergo a phase change) Calculate the standard entropy of vaporization of argon at its boiling point of 87.3 K given an enthalpy of vaporization of 6.5 kJ/mol. (Note another variation of this problem allows you to calculate a phase change temperature give the entropy and enthalpy of the phase change.)

Answer: $74 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

3. And now a refresher on calculating the ideal positional entropy at 0K. What is the entropy of a sample of a solid in which the molecules can take any one of three orientations with the same energy. Suppose there are 30 molecules in the sample.

Answer: $4.5 \times 10^{-22} \text{ J}\cdot\text{K}^{-1}$

4. One can successfully rank absolute molar entropies by looking at the complexity of the system. Complete the sentences below to create simply rules of thumb that will help you remember how to predict relative entropies.

As the temperature of a system increases, the molar entropy of a compound increases

As the pressure of a system increases, the molar entropy of a compound decreases

As the volume of a system increases, the molar entropy of a compound increases

As the number of particles in a system increases, the molar entropy of a compound increases

As the perfection of a compound's crystal structure increases, the molar entropy of a compound decreases

5. Apply the concepts in the question above to rank the molar entropy of the pairs of systems below:

(a) 1 mol CO_2 (g) at 25°C and 1 bar or 1 mol CO_2 (g) at 25°C and 3 bar;

(b) 1 mol He(g) at 25°C or 1 mol He(g) at 100°C in the same volume;

(c) Br_2 (l) or Br_2 (g) at the same temperature? Explain your conclusions.

Answer:

(a) CO_2 (g) at 1 bar, because disorder increases with volume

(b) He(g) at 100°C, because disorder increases with temperature;

(c) Br_2 (g), because the vapor state has greater disorder than the liquid state.

6. Tables of absolute entropies allow a ready comparison between compounds. Use the information below to determine which compound in a pair is the more ordered form,

(a) diamond or graphite at 25°C.

(b) nitrogen or oxygen at 25°C.

TABLE 7.3 Standard Molar Entropies at 25°C ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$)*

Gases	S_m°	Liquids	S_m°	Solids	S_m°
ammonia, NH_3	192.4	benzene, C_6H_6	173.3	calcium oxide, CaO	39.8
carbon dioxide, CO_2	213.7	ethanol, $\text{C}_2\text{H}_5\text{OH}$	160.7	calcium carbonate, CaCO_3^\dagger	92.9
hydrogen, H_2	130.7	water, H_2O	69.9	diamond, C	2.4
nitrogen, N_2	191.6			graphite, C	5.7
oxygen, O_2	205.1			lead, Pb	64.8

*Additional values are given in Appendix 2A.

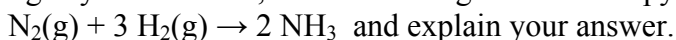
†Calcite.

Answer:

(a) diamond is the more ordered form because this is the most perfect of the crystalline forms of carbon

(b) Nitrogen in the most ordered form because it is smaller.

7. Without doing any calculations, estimate the sign of the entropy change for the reaction



Answer: Negative, because there is a net decrease in the number of moles of gas molecules]

8. Use data from Table 7.3 to calculate the standard entropy of the reaction in problem 7.

Answer: $-199 \text{ J}\cdot\text{K}^{-1}$]

9. Global changes in entropy. We know that reactions like the formation of ammonia from nitrogen and hydrogen actually do happen despite the decrease in entropy of the system. What is the reason?

Answer: The second law permits the entropy of a system to decrease as long as the entropy of the surroundings is sufficiently large to make the overall entropy of the universe increase.

10. Calculate the change in entropy of the surroundings when water freezes at $-10.^\circ\text{C}$; use $\Delta H_{\text{fus}}(\text{H}_2\text{O}) = 6.0 \text{ kJ}\cdot\text{mol}^{-1}$ at $-10.^\circ\text{C}$.

Answer: We can expect the entropy of the surroundings to increase when water freezes because the heat released stirs up the thermal motion of the atoms in the surroundings. To calculate the change in entropy of the surroundings when water freezes we write $\Delta H_{\text{freeze}} = -\Delta H_{\text{fus}} = -6.0 \text{ kJ}\cdot\text{mol}^{-1}$ and $T = (-10. + 273) \text{ K} = 263 \text{ K}$. Then $\Delta S_{\text{surr}} = -\Delta H/T = +23 \text{ kJ/K mol}$. and, shockingly, water freezes when it is cold.

11. Calculate the entropy change of the surroundings when 1.00 mol $\text{H}_2\text{O}(\text{l})$ vaporizes at 90°C and 1 bar. Take the enthalpy of vaporization of water as $40.7 \text{ kJ}\cdot\text{mol}^{-1}$.

Answer: $-112 \text{ J}\cdot\text{K}^{-1}$

12. Is the formation of hydrogen fluoride from its elements in their most stable forms spontaneous under standard conditions at 25°C ? For the reaction $\text{H}_2(\text{g}) + \text{F}_2(\text{g}) \rightarrow 2 \text{HF}(\text{g})$, $\Delta H^\circ = -542.2 \text{ kJ}$ and $\Delta S^\circ = +14.1 \text{ J}\cdot\text{K}^{-1}$.

Answer: $\Delta S_{\text{surr}} = +1819 \text{ J}\cdot\text{K}^{-1}$; therefore, $\Delta S_{\text{tot}} = +1833 \text{ J}\cdot\text{K}^{-1}$ and the reaction is spontaneous