Problems Chapter 18 (Entropy and Free Energy)

1. Compare the compounds in each set below and decide which is expected to have the higher entropy. Assume all are at the same temperature.
    a. HF (g), HCl (g) or HBr (g)
    b. NH_4Cl (s) or NH_4Cl (aq)
    c. C_2H_4 (g) or N_2 (g)
    d. NaCl (s) or NaCl (g)

2. When water vapors from hydrochloric acid and aqueous ammonia come in contact, they react, producing a white cloud of solid NH_4Cl.

$$HCl\ (g) + NH_3\ (g) \Leftrightarrow NH_4Cl\ (s)$$

    Defining the reactants and products as the system under study:
    a. Predict whether ΔS°_{system}, $\Delta S^\circ_{surroundings}$, $\Delta S^\circ_{universe}$, ΔH°_{rxn} and ΔG°_{rxn} (at 298 K) are greater than zero, equal to zero or less than zero and explain your prediction. Verify your predictions by calculating values for each of these quantities.
    b. Calculate the value of K for this reaction at 298 K.

3. Elemental boron, in the form of thin fibers, can be made by reducing a boron halide with H_2.

$$BCl_3\ (g) + 3/2\ H_2\ (g) \rightarrow B\ (s) + 3\ HCl\ (g)$$

    Calculate ΔH°_{rxn}, ΔS°_{rxn} and ΔG°_{rxn} at 25 ˚C for this reaction. Is this reaction predicted to be product-favored at equilibrium at 25 ˚C? If so, is it enthalpy- or entropy-driven? S˚ for B (s) is 5.86 J K^{-1} mol^{-1}.

4. Sulfur undergoes a phase transition between 80 and 100 ˚C.

$$S_8\ (rhombic) \rightarrow S_8\ (monoclinic)$$
$$\Delta H^\circ_{rxn} = 3.213\ kJ\ mol^{-1}$$
$$\Delta S^\circ_{rxn} = 8.7\ J\ K^{-1}\ mol^{-1}$$

    a. Estimate ΔG°_{rxn} for the transition at 80.0 ˚C and 110.0 ˚C. What do these results tell you about the stability of the two forms of sulfur at each of these temperatures?
    b. Calculate the temperature at which $\Delta G^\circ_{rxn} = 0$. What is the significance of this temperature?

5. At 298 K, 1.00 mol BrCl (g) is introduced into a 10.0 L vessel, and equilibrium is established in the reaction BrCl (g) $\Leftrightarrow$ ½ Br_2 (g) + ½ Cl_2 (g). Calculate the amounts of each of the three gases present when equilibrium is established. For BrCl (g), $\Delta G^\circ_f = -0.98$ kJ mol^{-1}.

6. The following table shows the enthalpies and Gibbs free energies of formation of three metal oxides at 25 ˚C.

	ΔH_f°, kJ mol^{-1}	ΔG_f°, kJ mol^{-1}
PbO(red)	−219.0	−188.9
Ag_2O	−31.05	−11.20
ZnO	−348.3	−318.3

   a. Which of these oxides can be most readily decomposed to the free metal and O_2 (g)?
   b. For the oxide that is most easily decomposed, to what temperature must it be heated to produce O_2 (g) at 1.00 atm pressure?

7. The following data are given for the two solid forms of HgI_2 at 298 K.

	ΔH_f°, kJ mol^{-1}	ΔG_f°, kJ mol^{-1}	S°, J mol^{-1} K^{-1}
HgI_2(red)	−105.4	−101.7	180
HgI_2(yellow)	−102.9	(?)	(?)

   Estimate values for the two missing entries. To do that, assume that for the transition HgI_2 (red) → HgI_2 (yellow), the values of ΔH°_{rxn} and ΔS°_{rxn} at 25 ˚C have the same values that they do at the equilibrium temperature of 127 ˚C.

8. Oxides of nitrogen are produced at high-temperature combustion processes. The essential reaction is N_2 (g) + O_2 (g) ⇔ 2 NO (g). At what approximate temperature will an equimolar mixture of N_2 (g) and O_2 (g) be 1.0% converted to NO (g)?

9. For the majority of compounds, the value of ΔG°_f is more positive (or less negative) than the value of ΔH°_f.
   a. Explain this observation using NH_3 (g) and CCl_4 (l) as examples.
   b. An exception to this observation is CO (g). Explain the trend in the ΔH°_f and ΔG°_f values for this molecule.

10. Use the following data, as appropriate, to estimate the molarity of a saturated aqueous solution of $Sr(IO_3)_2$ at 298 K.

	ΔH°_f (kJ mol^{-1})	**S° (J mol^{-1} K^{-1})**
$Sr(IO_3)_2$ (s)	–1019.2	234
Sr^{2+} (aq)	–545.8	–32.6
IO_3^- (aq)	–221.3	118.4

11. Indicate whether each of the following statements is true or false. If it is false, correct it.
    a. The feasibility of manufacturing NH_3 from N_2 and H_2 depends entirely on the value of ΔH for the process N_2 (g) + 3 H_2 (g) → 2 NH_3 (g).
    b. The reaction of Na (s) with Cl_2 (g) to form NaCl (s) is a product-favored process.
    c. Spontaneous processes in general require that work is done to force them to proceed.
    d. Spontaneous processes are those that are exothermic and that lead to a higher degree of order in the system.

12. For each of the following processes, indicate whether the signs of ΔS and ΔH are expected to be positive, negative or about zero.
    a. A solid sublimes.
    b. The temperature of a sample of Co (s) is lowered from 60 ˚C to 25 ˚C.
    c. Ethyl alcohol evaporates from a beaker.
    d. A diatomic molecule dissociates into atoms.
    e. A piece of charcoal is combusted to form CO_2 (g) and H_2O (g).

13. Consider the reaction occurring at 298 K:
    N_2O (g) + NO_2 (g) ⇔ 3 NO (g)
    a. Show that this reaction is not product-favored under standard conditions by calculating ΔG°_{rxn}.
    b. If a reaction mixture contains only N_2O and NO_2 at partial pressures of 1.0 atm each, the reaction will be spontaneous until some NO forms in the mixture. What maximum partial pressure of NO builds up before the reaction ceases to be spontaneous?
    c. Can the reaction be made more product-favored by an increase or decrease in temperature? If so, what temperature is required to make the reaction product-favored?

14. Living organisms use energy from the metabolism of food to create an energy-rich molecule called adenosine triphosphate (ATP). ATP acts as an energy source for a variety of reactions that the living organisms must carry out to survive. ATP provides energy through its hydrolysis, which can be symbolized as follows:

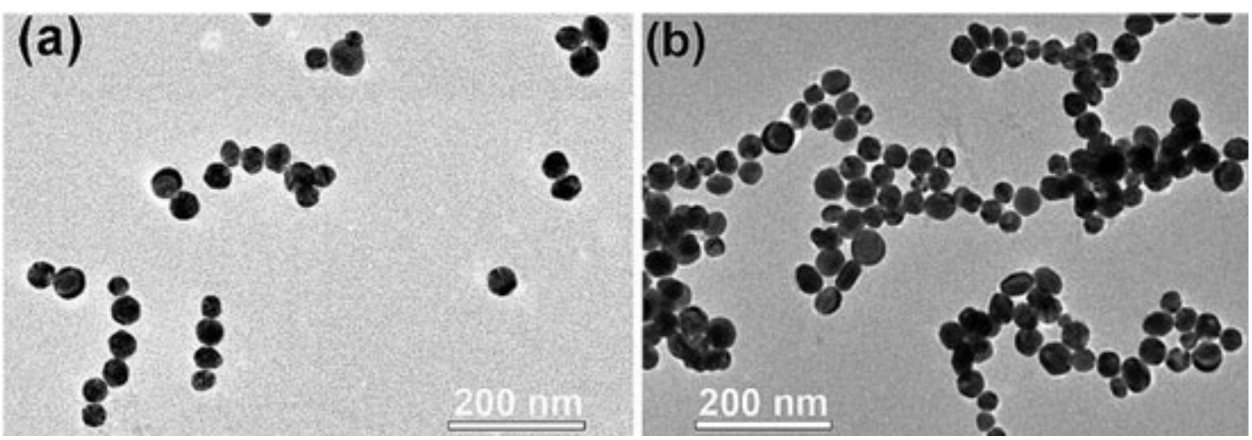
    ATP (aq) + H_2O (l) → ADP (aq) P_i (aq) $\Delta G^\circ_{rxn} = -30.5$ kJ

    where ADP represents adenosine diphosphate and P_i represents an inorganic phosphate group (such as HPO_4^{2-}).

    a. Calculate the equilibrium constant, K, for the given reaction at 298 K.
    b. The free energy obtained from the oxidation (reaction with oxygen) of glucose ($C_6H_{12}O_6$) to form carbon dioxide and water can be used to re-form ATP by driving the given reaction in reverse. Calculate the standard Gibbs free energy change for the oxidation of glucose and estimate the maximum number of moles of ATP that can be formed by the oxidation of one mole of glucose. For $C_6H_{12}O_6$ (s), $\Delta G^\circ_f = -910.4$ kJ mol^{-1}.

R. Lee Penn: a leader in the field of nanoscience

Nanomaterials – materials that have at least one dimension in the range of 1-100 nm – have been in the forefront of modern research. Due to their unique properties stemming from their unusually small size, nanomaterials have broad applications, such as computer and television displays, electronics, sensors, filters, catalysts and many more. For a nanomaterial to form, atoms and molecules must often spontaneously organize themselves into larger (but still nanosized) particles through a process called self-assembly. Such a process will be spontaneous if the Gibbs free energy ($\Delta G = \Delta H - T\Delta S$) associated with it is negative. As larger, more organized, structures form from smaller subunits, entropy decreases ($\Delta S < 0$ and $-T\Delta S > 0$). Therefore, to achieve $\Delta G < 0$, the process must be exothermic ($\Delta H < 0$) – the intermolecular forces within the nanoparticle must be stronger than those in the subunits forming it.



Gold nanoparticles self-assemble into long chains when bombarded with electrons

R. Lee Penn is a nonbinary chemistry professor at the University of Minnesota and a leading figure in the fields of nanoscience, crystal growth, materials science and environmental science/geochemistry. They study growth mechanisms of inorganic nanoparticles, such as metal oxides, perovskites, silver nanostructures and metal-organic frameworks, as well as the impact of nanoparticles on the environment. To characterize the materials, they use advanced imaging techniques such as scanning electron microscopy (since visible light has wavelengths on the order of a few hundreds of nanometers, optical microscopy does not provide the resolution required to probe nanomaterials). Penn is dedicated to promoting access of underrepresented groups to science fields and advocating for marginalized communities. They provide lectures and workshops across USA on various issues that affect women and LGBTQ+ individuals, as well as mentor and advise LGBTQ+ students through dedicated programs at the University of Minnesota. Penn has a distinguished career full of publications in high-profile peer-reviewed academic journals, collaborations with leaders in the field of inorganic chemistry and awards for their excellence in both research and teaching.

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