Spontaneity, Entropy, and Free Energy
Part I

Predicting Spontaneity (qualitatively)

1. Predict if the process is thermodynamically favored or not.
   (a) Water evaporating from a puddle in summer.

   (b) A soft-boiled egg becoming raw and releasing heat.

   (c) A satellite falling to Earth.

   (d) Water decomposing at room temperature to form hydrogen and oxygen gas.

2. Predict the sign of ΔS_{sys} for each of the following and justify the answer:

Remember: (+) entropy = more arrangements (more disorder);
(-) entropy = less arrangements (more order)

   (a) A piece of wax melting.

   (b) Silver chloride precipitating from solution.

   (c) Dew forming.

   (d) Gasoline vapors mixing with air in a car engine.

   (e) Hot air expanding.

3. Without looking in the Appendix, predict the sign of ΔS_{sys} for the following systems. Justify your answer. Compare states of matter and think about which state has more movement, more volume or more arrangements.

   (a) $2K(s) + F_2(g) \rightarrow 2KF(s)$

   (b) $NH_3(g) + HBr(g) \rightarrow NH_4Br(s)$

   (c) $NaClO_3(s) \rightarrow Na^+(aq) + ClO_3^-(aq)$

   (d) $H_2S(g) + \frac{1}{2} O_2(g) \rightarrow 1/8\ S_8(s) + H_2O(l)$

   (e) $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O(l)$

4. Predict the sign of ΔS for the following:

   (a) $O_2(aq)$ at 303 K and 1 atm $\rightarrow$ $O_2(g)$ at 303 K and 1 atm.

   (b) $O_2(g)$ (V = 1.0 L, P = 1 atm) $\rightarrow$ $O_2(g)$ (V = 0.10 L, P = 10 atm)

5. Which pair has the greater molar entropy:

   (a) butane, $CH_3CH_2CH_2CH_3(g)$ or butene, $CH_3CH{=}{=}CHCH_3$ (g)

   (b) Ne(g) or Xe(g)

   (c) Na(s) or K(s)

   (d) $KClO_3(s)$ or $KClO_3(aq)$

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6.	ΔH^o_f (kJ/mol)	S^o (J/mol)	ΔG^o_f (kJ/mol)
C_3H_8	-104	270	-24
O_2	0	205	0
CO_2	-393.5	214	-394
H_2O	-242	189	-229

(a) Balance the equation for the combustion of propane gas.

(b) Calculate ΔH^o.

(c) Calculate ΔS^o.

(d) Calculate ΔG^o using two methods, verifying that free energy is a state function.
Hopefully you remembered to convert S to kJ from J!

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7. Consider the following equation

$O_3(g) + NO(g) \rightarrow O_2(g) + NO_2(g)$

(a) Referring to the data in the table below, calculate the standard enthalpy change, ΔH^o, for the reaction at 25 °C. Be sure to show your work.

	$O_3(g)$	$NO(g)$	$NO_2(g)$
ΔH^o_f at 25 °C	143	90.	33

(b) Make a qualitative prediction about the magnitude of the standard entropy change, ΔS^o, for the reaction at 25 °C. Justify your answer.

(c) On the basis of your answers to part (a) and (b), predict the sign for the standard free energy change, ΔG^o, for the reaction at 25 °C. Explain your reasoning.

(d) Use the information in the table below to write the rate-law for the reaction, and explain how you obtained your answer.

Number Experiment	Initial $[O_3]$ (mol/L)	Initial [NO] (mol/L)	Init Rate of Formation of NO_2 (mol $L^{-1}s^{-1}$)
1	0.0010	0.0010	1x
2	0.0010	0.0020	2x
3	0.0020	0.0010	2x
4	0.0020	0.0020	4x

(e) Identify the step that must be the slowest in order for this mechanism to be consistent with the rate-law expression derived in part (d). Explain.

Step I: $O_3 + NO \rightarrow O + NO_3$

Step II: $O + O_3 \rightarrow 2\ O_2$

Step III: $NO_3 + NO \rightarrow 2\ NO_2$