

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) $2\text{K(s)} + \text{F}_2(\text{g}) \rightarrow 2\text{KF(s)}$
- (b) $\text{NH}_3(\text{g}) + \text{HBr}(\text{g}) \rightarrow \text{NH}_4\text{Br(s)}$
- (c) $\text{NaClO}_3(\text{s}) \rightarrow \text{Na}^+(\text{aq}) + \text{ClO}_3^-(\text{aq})$
- (d) $\text{H}_2\text{S}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \rightarrow \frac{1}{8} \text{S}_8(\text{s}) + \text{H}_2\text{O(l)}$
- (e) $\text{HCl}(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCl}(\text{aq}) + \text{H}_2\text{O(l)}$

4. Predict the sign of ΔS for the following:

- (a) $\text{O}_2(\text{aq})$ at 303 K and 1 atm \rightarrow $\text{O}_2(\text{g})$ at 303 K and 1 atm.
- (b) $\text{O}_2(\text{g})$ ($V = 1.0 \text{ L}$, $P = 1 \text{ atm}$) \rightarrow $\text{O}_2(\text{g})$ ($V = 0.10 \text{ L}$, $P = 10 \text{ atm}$)

5. Which pair has the greater molar entropy:

- (a) butane, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3(\text{g})$ or butene, $\text{CH}_3\text{CH}=\text{CHCH}_3(\text{g})$
- (b) $\text{Ne}(\text{g})$ or $\text{Xe}(\text{g})$
- (c) $\text{Na}(\text{s})$ or $\text{K}(\text{s})$
- (d) $\text{KClO}_3(\text{s})$ or $\text{KClO}_3(\text{aq})$

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6.	ΔH_f° (kJ/mol)	S° (J/mol)	ΔG_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° .

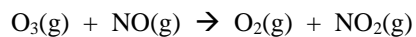
(c) Calculate ΔS° .

(d) Calculate ΔG° 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



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

	$\text{O}_3(\text{g})$	$\text{NO}(\text{g})$	$\text{NO}_2(\text{g})$
ΔH°_f at 25 °C	143	90.	33

- (b) Make a qualitative prediction about the magnitude of the standard entropy change, ΔS° , 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° , 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 $[\text{O}_3]$ (mol/L)	Initial $[\text{NO}]$ (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

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- (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.

