

Show all work with units and correct significant figures. When you decide whether a process is thermodynamically favored, state the sign of ΔG° (or E°) and explain what it means.

Constants	$R = 8.314 \text{ J/(mol}\cdot\text{K)}$	$F = 96,485 \text{ C/mol e}^-$	$1 \text{ A} = 1 \text{ C/s}$
	$1 \text{ V} = 1 \text{ J/C}$	$1 \text{ kJ} = 1000 \text{ J}$	$K = ^\circ\text{C} + 273$
Equations	$\Delta S^\circ = \Sigma S^\circ(\text{products}) - \Sigma S^\circ(\text{reactants})$	$\Delta G^\circ = \Sigma \Delta G_f^\circ(\text{products}) - \Sigma \Delta G_f^\circ(\text{reactants})$	$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
	$\Delta G^\circ = -RT \ln K$	$\Delta G^\circ = -nFE^\circ$	$E = E^\circ - (RT/nF) \ln Q$
	$K = e^{-\Delta G^\circ/RT}$	$I = q/t$	$q = (\text{mol e}^-) \times F$

Part 1. Entropy (Topics 9.1 to 9.2)

1. Predict the sign of ΔS° for each process and give a short reason.

Process	Sign of ΔS°	Reason
$\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}$		
$2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$		
$\text{CaCO}_3(\text{s}) \rightarrow \text{CaO(s)} + \text{CO}_2(\text{g})$		
$\text{NaCl(s)} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$		
He(g) is compressed from 2.0 L to 1.0 L at constant temperature		
Ar(g) is heated from 300 K to 400 K		

2. Use the standard molar entropies below for the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$.

Substance	$\text{N}_2(\text{g})$	$\text{H}_2(\text{g})$	$\text{NH}_3(\text{g})$
$S^\circ \text{ (J/(mol}\cdot\text{K))}$	191.6	130.7	192.5

- (a) Calculate ΔS° for the reaction.

- (b) Explain why the sign of your answer makes sense.

3. Decide whether each statement is true or false. If it is false, rewrite it so it is true.

- (a) Every exothermic reaction has a positive ΔS° .

- (b) A gas that expands into a larger volume at constant temperature gains entropy.

- (c) The entropy of a substance decreases as its temperature increases.

Part 2. Gibbs Free Energy and Thermodynamic Favorability (Topic 9.3)

4. Complete the table. The first row is done for you.

Sign of ΔH°	Sign of ΔS°	Thermodynamically favored ($\Delta G^\circ < 0$) at:
–	+	all temperatures
+	–	
+	+	
–	–	

5. For $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$, $\Delta H^\circ = -114.1 \text{ kJ/mol}_{\text{rxn}}$ and $\Delta S^\circ = -146.5 \text{ J/(mol}_{\text{rxn}} \cdot \text{K})$.

(a) Calculate ΔG° at 298 K. Is the reaction thermodynamically favored at 298 K?

(b) Above what temperature is the reaction no longer thermodynamically favored?

6. Use the standard free energies of formation to calculate ΔG° for $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$.

Substance	$\text{CH}_4(\text{g})$	$\text{O}_2(\text{g})$	$\text{CO}_2(\text{g})$	$\text{H}_2\text{O}(\text{l})$
ΔG°_f (kJ/mol)	–50.8	0	–394.4	–237.1

7. Liquid water freezes at -10°C but not at $+10^\circ\text{C}$. Use the signs of ΔH° and ΔS° for freezing to explain why.

Part 3. Thermodynamic and Kinetic Control (Topic 9.4)

8. For $\text{C(s, diamond)} \rightarrow \text{C(s, graphite)}$, $\Delta G^\circ = -2.9 \text{ kJ/mol}_{\text{rxn}}$ at 298 K, yet diamonds do not turn into graphite on any human timescale.

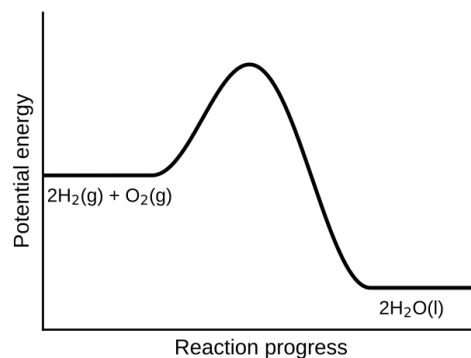
(a) Explain why the reaction does not happen at a measurable rate.

(b) A student says, "Diamond does not change because the system is at equilibrium." Explain why the student is wrong.

9. A mixture of $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$ can sit for years without reacting, but a spark makes it explode. For $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$, $\Delta G^\circ = -474.2 \text{ kJ/mol}_{\text{rxn}}$.

(a) On the energy diagram, label the activation energy (E_a) and ΔH for the reaction.

(b) Explain why the mixture does not react on its own, and what the spark does.



Part 4. Free Energy and Equilibrium (Topic 9.5)

10. For the ionization of acetic acid at 298 K, $K_a = 1.8 \times 10^{-5}$. Calculate ΔG° and explain what its sign tells you.

11. For $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$ at 298 K, $\Delta G^\circ = -32.9 \text{ kJ/mol}_{\text{rxn}}$. Calculate K at 298 K.

12. Complete the table for three reactions at 298 K.

ΔG°	Is $K \gg 1$, ≈ 1 , or $\ll 1$?	Favored at equilibrium
$-50 \text{ kJ/mol}_{\text{rxn}}$		
$+0.5 \text{ kJ/mol}_{\text{rxn}}$		
$+50 \text{ kJ/mol}_{\text{rxn}}$		

Part 5. Free Energy of Dissolution and Coupled Reactions (Topics 9.6 to 9.7)

13. Ammonium nitrate, $\text{NH}_4\text{NO}_3(\text{s})$, dissolves readily in water, and the solution becomes colder.

(a) What is the sign of ΔH° for dissolving NH_4NO_3 ? Explain how you know.

(b) Complete the table for two of the steps in dissolving an ionic solid.

Step	Sign of ΔH	Effect on entropy
Ions are separated from the crystal lattice		
Ions become surrounded by attracted water molecules (ion-dipole attractions form)		

(c) Since $\Delta H^\circ > 0$, explain how dissolving NH_4NO_3 can still be thermodynamically favored at room temperature.

(d) Explain why it is hard to predict the sign of ΔG° for dissolving a salt just by looking at its formula.

14. Cells make glucose-6-phosphate by coupling two reactions.

Reaction	ΔG° (kJ/mol _{rxn})
glucose + phosphate $\rightarrow$ glucose-6-phosphate + H_2O	+13.8
$\text{ATP} + \text{H}_2\text{O} \rightarrow \text{ADP} + \text{phosphate}$	-30.5

(a) Write the overall reaction and calculate ΔG° for it. Is the overall reaction thermodynamically favored?

(b) Identify the common intermediates that connect the two reactions.

15. Each process below is thermodynamically unfavored. Name the external energy source that makes it happen.

(a) Photosynthesis: $6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g})$, $\Delta G^\circ = +2880 \text{ kJ/mol}_{\text{rxn}}$

(b) Recharging a phone battery

Part 6. Galvanic and Electrolytic Cells (Topics 9.8 to 9.9)

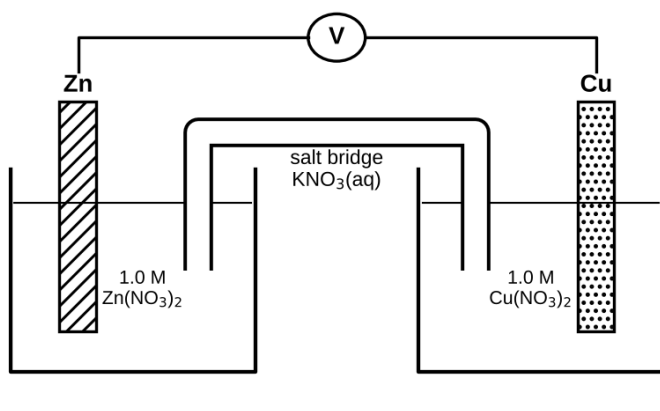
16. Complete the table comparing the two types of electrochemical cells.

	Galvanic cell	Electrolytic cell
Sign of ΔG° for the cell reaction		
Sign of E°_{cell}		
Needs an external power source?		
Electrode where oxidation occurs		

Use these standard reduction potentials (298 K) for Questions 17 to 20.

Half-reaction	E° (V)
$\text{Cl}_2(\text{g}) + 2\text{e}^- \rightarrow 2\text{Cl}^-(\text{aq})$	+1.36
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+0.80
$\text{Cu}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.34
$2\text{H}^+(\text{aq}) + 2\text{e}^- \rightarrow \text{H}_2(\text{g})$	0.00
$\text{Pb}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Pb}(\text{s})$	-0.13
$\text{Ni}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.25
$\text{Zn}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.76

17. The galvanic cell below is made of a zinc electrode in 1.0 M $\text{Zn}(\text{NO}_3)_2$ and a copper electrode in 1.0 M $\text{Cu}(\text{NO}_3)_2$.



- Write the half-reaction that occurs at each electrode. Label the anode and the cathode on the diagram.
- On the diagram, draw an arrow showing the direction of electron flow in the wire. Then show which way K^+ and NO_3^- ions move in the salt bridge.
- Calculate E°_{cell} .
- What happens to the mass of each electrode as the cell runs?
- Predict what happens to the voltage if the salt bridge is removed. Explain.

Part 7. Cell Potential, Free Energy, and Nonstandard Conditions (Topics 9.9 to 9.10)

18. Consider the reaction $2\text{Ag}^+(\text{aq}) + \text{Ni}(\text{s}) \rightarrow 2\text{Ag}(\text{s}) + \text{Ni}^{2+}(\text{aq})$.

- Calculate E° for the reaction.
- Calculate ΔG° in $\text{kJ/mol}_{\text{rxn}}$. Is the reaction thermodynamically favored?

19. Is $\text{Pb(s)} + \text{Zn}^{2+}(\text{aq}) \rightarrow \text{Pb}^{2+}(\text{aq}) + \text{Zn(s)}$ thermodynamically favored under standard conditions? If not, what would be needed to make it happen?

20. The Zn/Cu cell from Question 17 starts at standard conditions, $\text{Zn(s)} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu(s)}$. For each change, predict the effect on the cell voltage and explain using Q.

Change	Effect on E (increase, decrease, or no change)	Reason
$[\text{Cu}^{2+}]$ is increased to 2.0 M		
$[\text{Zn}^{2+}]$ is increased to 2.0 M		
The cell runs for a long time		
A larger Zn electrode is used		

21. A concentration cell has two Cu electrodes, one in 0.010 M Cu^{2+} and one in 1.0 M Cu^{2+} . E° for this cell is 0 V. Explain why the cell still produces a voltage, and identify which electrode is the anode.

22. True or false? If false, correct the statement.

(a) A cell reaction with $E^\circ > 0$ has $K > 1$.

(b) Doubling every coefficient in a cell reaction doubles E° .

Part 8. Electrolysis and Faraday's Law (Topic 9.11)

23. A current of 2.50 A passes through a AgNO_3 solution for 45.0 min. What mass of Ag(s) plates out at the cathode?

24. How many minutes does it take to plate 5.00 g of Cu(s) from a Cu^{2+} solution using a 3.00 A current?

25. Two electrolytic cells are connected in series, so 0.200 mol of electrons passes through each. One contains $\text{Ag}^+(\text{aq})$ and the other contains $\text{Cu}^{2+}(\text{aq})$. Calculate the mass of metal deposited in each cell and explain why the moles of metal are different.