

AP CHEMISTRY

UNIT 9

Thermodynamics and Electrochemistry



7–9%

AP EXAM WEIGHTING



~10–13

CLASS PERIODS

Thermodynamics and Electrochemistry

ESSENTIAL QUESTIONS

- Why do some chemical reactions occur without intervention, but others require the input of energy?
- How can we determine the conditions under which a chemical or physical transformation is likely to occur?
- How is electrical energy generated using chemical reactions?

Developing Understanding

This unit allows students to connect principles and calculations across Units 1–8. The thermodynamics of a chemical reaction is connected to both the structural aspects of the reaction and the macroscopic outcomes of the reaction. All changes in matter involve some form of energy change. One key determinant of chemical transformations is the change in potential energy that results from changes in electrostatic forces. Chemical systems undergo three main processes that change their energy: heating/cooling, phase transitions, and chemical reactions. Applying the laws of thermodynamics will allow students to describe the essential role of energy and explain and predict the direction of changes in matter.

Building the Science Practices

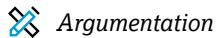
5.F | 6.D | 6.E

To achieve success in AP Chemistry and in Unit 9 specifically, students must connect principles and calculations across the areas of kinetics, thermodynamics, equilibrium, and electrochemistry to explain and support claims about what is happening in chemical systems. Sometimes support of such claims comes from students being able to estimate an approximate value of a required characteristic of a chemical system rather than use a routine application of an algorithm.

Students are introduced to entropy as a factor that is necessary to explain why some endothermic reactions occur in spite of the higher energy that products may have in these changes. Students will use particulate representations and graphical distribution of kinetic energy to describe the increase in entropy with increasing temperature. In addition, students will explore how to use Gibbs free energy for determining the thermodynamic favorability by considering the change in both enthalpy and entropy. Students will use the concepts of thermodynamics to generate more comprehensive claims about what is happening in a galvanic or electrolytic cell.

Preparing for the AP Exam

On the AP Exam, students must be able to provide an appropriate explanation of the connection between entropy, enthalpy, and Gibbs free energy and the thermodynamic favorability of a chemical reaction. Students often struggle with questions that require them to reason about whether enthalpy, entropy, or both drive a reaction. They will state that both enthalpy and entropy drive the reaction by using the equation for Gibbs free energy instead of reasoning about which might be more of a driving factor than the other. Further, some students fail to connect macroscopic observational data to the concepts of entropy and enthalpy to support claims about which concept was driving the reaction. Teachers can ensure that students understand that the first step in making thermodynamic favorability predictions is to define and interrelate enthalpy, entropy, and Gibbs free energy in relation to driving chemical or physical processes. Students should be shown how the concepts of kinetics, equilibrium, and thermodynamics are connected in order to explain why thermodynamically favorable reactions might produce small concentrations of product and why unfavorable reactions can produce large concentrations of product.

SUGGESTED SKILL**6.C**

Support a claim with evidence from representations or models at the particulate level, such as the structure of atoms and/or molecules.

**AVAILABLE RESOURCES**

- Classroom Resource > [Units in Thermochemical Calculations](#)
- The Exam > [2019 Chief Reader Report](#)

TOPIC 9.1

Introduction to Entropy

Required Course Content

LEARNING OBJECTIVE**9.1.A**

Identify the sign and relative magnitude of the entropy change associated with chemical or physical processes.

ESSENTIAL KNOWLEDGE**9.1.A.1**

Entropy increases when matter becomes more dispersed. For example, the phase change from solid to liquid or from liquid to gas results in a dispersal of matter as the individual particles become freer to move and generally occupy a larger volume. Similarly, for a gas, the entropy increases when there is an increase in volume (at constant temperature), and the gas molecules are able to move within a larger space. For reactions involving gas-phase reactants or products, the entropy generally increases when the total number of moles of gas-phase products is greater than the total number of moles of gas-phase reactants.

9.1.A.2

Entropy increases when energy is dispersed. According to kinetic molecular theory (KMT), the distribution of kinetic energy among the particles of a gas broadens as the temperature increases. As a result, the entropy of the system increases with an increase in temperature.

TOPIC 9.2

Absolute Entropy and Entropy Change

Required Course Content

LEARNING OBJECTIVE**9.2.A**

Calculate the standard entropy change for a chemical or physical process based on the absolute entropies (standard molar entropies) of the species involved in the process.

ESSENTIAL KNOWLEDGE**9.2.A.1**

The entropy change for a process can be calculated from the absolute entropies of the species involved before and after the process occurs.

$$\text{EQN: } \Delta S_{\text{reaction}}^{\circ} = \Sigma S_{\text{products}}^{\circ} - \Sigma S_{\text{reactants}}^{\circ}$$

SUGGESTED SKILL

 *Mathematical Routines*

5.F

Calculate, estimate, or predict an unknown quantity from known quantities by selecting and following a logical computational pathway and attending to precision (e.g., performing dimensional analysis and attending to significant figures).

**AVAILABLE RESOURCES**

- Classroom Resource > [Units in Thermochemical Calculations](#)
- The Exam > [2019 Chief Reader Report](#)

SUGGESTED SKILL

 Argumentation**6.E**

Provide reasoning to justify a claim using connections between particulate and macroscopic scales or levels.



AVAILABLE RESOURCES

- The Exam > [2017 Chief Reader Report](#)
- The Exam > [2019 Chief Reader Report](#)

TOPIC 9.3

Gibbs Free Energy and Thermodynamic Favorability

Required Course Content

LEARNING OBJECTIVE**9.3.A**

Explain whether a physical or chemical process is thermodynamically favored based on an evaluation of ΔG° .

ESSENTIAL KNOWLEDGE**9.3.A.1**

The Gibbs free energy change for a chemical process in which all the reactants and products are present in a standard state (as pure substances, as solutions of 1.0 M concentration, or as gases at a pressure of 1.0 atm (or 1.0 bar)) is given the symbol ΔG° .

9.3.A.2

The standard Gibbs free energy change for a chemical or physical process is a measure of thermodynamic favorability. Historically, the term "spontaneous" has been used to describe processes for which $\Delta G^\circ < 0$. The phrase "thermodynamically favored" is preferred instead so that common misunderstandings (equating "spontaneous" with "suddenly" or "without cause") can be avoided. When $\Delta G^\circ < 0$ for the process, it is said to be thermodynamically favored.

9.3.A.3

The standard Gibbs free energy change for a physical or chemical process may also be determined from the standard Gibbs free energy of formation of the reactants and products.

$$\text{EQN: } \Delta G_{\text{reaction}}^\circ = \sum \Delta G_f^\circ_{\text{products}} - \sum \Delta G_f^\circ_{\text{reactants}}$$

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LEARNING OBJECTIVE**9.3.A**

Explain whether a physical or chemical process is thermodynamically favored based on an evaluation of ΔG° .

ESSENTIAL KNOWLEDGE**9.3.A.4**

In some cases, it is necessary to consider both enthalpy and entropy to determine if a process will be thermodynamically favored. The freezing of water and the dissolution of sodium nitrate are examples of such phenomena.

9.3.A.5

Knowing the values of ΔH° and ΔS° for a process at a given temperature allows ΔG° to be calculated directly.

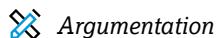
$$\text{EQN: } \Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

9.3.A.6

In general, the temperature conditions for a process to be thermodynamically favored ($\Delta G^\circ < 0$) can be predicted from the signs of ΔH° and ΔS° as shown in the table below:

ΔH°	ΔS°	Symbols	$\Delta G^\circ < 0$, favored at:
< 0	> 0	<>	all T
> 0	< 0	><	no T
> 0	> 0	>>	high T
< 0	< 0	<<	low T

In cases where $\Delta H^\circ < 0$ and $\Delta S^\circ > 0$, no calculation of ΔG° is necessary to determine that the process is thermodynamically favored ($\Delta G^\circ < 0$). In cases where $\Delta H^\circ > 0$ and $\Delta S^\circ < 0$, no calculation of ΔG° is necessary to determine that the process is thermodynamically unfavored ($\Delta G^\circ > 0$).

SUGGESTED SKILL**6.E**

Provide reasoning to justify a claim using connections between particulate and macroscopic scales or levels.

TOPIC 9.4

Thermodynamic and Kinetic Control

Required Course Content

LEARNING OBJECTIVE**9.4.A**

Explain, in terms of kinetics, why a thermodynamically favored reaction might not occur at a measurable rate.

ESSENTIAL KNOWLEDGE**9.4.A.1**

Many processes that are thermodynamically favored do not occur to any measurable extent, or they occur at extremely slow rates.

9.4.A.2

Processes that are thermodynamically favored, but do not proceed at a measurable rate, are under “kinetic control.” High activation energy is a common reason for a process to be under kinetic control. The fact that a process does not proceed at a noticeable rate does not mean that the chemical system is at equilibrium. If a process is known to be thermodynamically favored, and yet does not occur at a measurable rate, it is reasonable to conclude that the process is under kinetic control.

TOPIC 9.5

Free Energy and Equilibrium

SUGGESTED SKILL Argumentation**6.D**

Provide reasoning to justify a claim using chemical principles or laws, or using mathematical justification.

Required Course Content

LEARNING OBJECTIVE**9.5.A**

Explain whether a process is thermodynamically favored using the relationships between K , ΔG° , and T .

ESSENTIAL KNOWLEDGE**9.5.A.1**

The phrase “thermodynamically favored” ($\Delta G^\circ < 0$) means that the products are favored at equilibrium ($K > 1$) under standard conditions.

9.5.A.2

The equilibrium constant is related to free energy by the equations

$$\text{EQN: } K = e^{-\Delta G^\circ / RT}$$

and

$$\text{EQN: } \Delta G^\circ = -RT \ln K.$$

9.5.A.3

Connections between K and ΔG° can be made qualitatively through estimation. When ΔG° is near zero, the equilibrium constant will be close to 1. When ΔG° is much larger or much smaller than RT , the value of K deviates strongly from 1.

9.5.A.4

Processes with $\Delta G^\circ < 0$ favor products (i.e., $K > 1$) and those with $\Delta G^\circ > 0$ favor reactants (i.e., $K < 1$).

SUGGESTED SKILL *Model Analysis***4.D**

Explain the degree to which a model or representation describes the connection between particulate-level properties and macroscopic properties.

TOPIC 9.6

Free Energy of Dissolution

Required Course Content

LEARNING OBJECTIVE**9.6.A**

Explain the relationship between the solubility of a salt and changes in the enthalpy and entropy that occur in the dissolution process.

ESSENTIAL KNOWLEDGE**9.6.A.1**

The free energy change (ΔG°) for dissolution of a substance reflects a number of factors: the breaking of the intermolecular interactions that hold the solid together, the reorganization of the solvent around the dissolved species, and the interaction of the dissolved species with the solvent. It is possible to estimate the sign and relative magnitude of the enthalpic and entropic contributions to each of these factors. However, making predictions for the total change in free energy of dissolution can be challenging due to the cancellations among the free energies associated with the three factors cited.

TOPIC 9.7
Coupled Reactions**SUGGESTED SKILL**
 *Model Analysis***4.D**

Explain the degree to which a model or representation describes the connection between particulate-level properties and macroscopic properties.

Required Course Content**LEARNING OBJECTIVE****9.7.A**

Explain the relationship between external sources of energy or coupled reactions and their ability to drive thermodynamically unfavorable processes.

ESSENTIAL KNOWLEDGE**9.7.A.1**

An external source of energy can be used to make a thermodynamically unfavorable process occur. Examples include:

- i. Electrical energy to drive an electrolytic cell or charge a battery.
- ii. Light to drive the overall conversion of carbon dioxide to glucose in photosynthesis.

9.7.A.2

A desired product can be formed by coupling a thermodynamically unfavorable reaction that produces that product to a favorable reaction (e.g., the conversion of *ATP* to *ADP* in biological systems). In the coupled system, the individual reactions share one or more common intermediates. The sum of the individual reactions produces an overall reaction that achieves the desired outcome and has $\Delta G^\circ < 0$.

SUGGESTED SKILL **Question and Method****2.F**

Explain how modifications to an experimental procedure will alter results.

TOPIC 9.8

Galvanic (Voltaic) and Electrolytic Cells

Required Course Content

LEARNING OBJECTIVE**9.8.A**

Explain the relationship between the physical components of an electrochemical cell and the overall operational principles of the cell.

ESSENTIAL KNOWLEDGE**9.8.A.1**

Each component of an electrochemical cell (electrodes, solutions in the half-cells, salt bridge, voltage/current measuring device) plays a specific role in the overall functioning of the cell. The operational characteristics of the cell (galvanic vs. electrolytic, direction of electron flow, reactions occurring in each half-cell, change in electrode mass, evolution of a gas at an electrode, ion flow through the salt bridge) can be described at both the macroscopic and particulate levels.

9.8.A.2

Galvanic, sometimes called voltaic, cells involve a thermodynamically favored reaction, whereas electrolytic cells involve a thermodynamically unfavored reaction. Visual representations of galvanic and electrolytic cells are tools of analysis to identify where half-reactions occur and in what direction current flows.

9.8.A.3

For all electrochemical cells, oxidation occurs at the anode and reduction occurs at the cathode.

Exclusion Statement: Labeling an electrode as positive or negative will not be assessed on the AP Exam.

TOPIC 9.9

Cell Potential and Free Energy

SUGGESTED SKILL Mathematical Routines**5.F**

Calculate, estimate, or predict an unknown quantity from known quantities by selecting and following a logical computational pathway and attending to precision (e.g., performing dimensional analysis and attending to significant figures).

**AVAILABLE RESOURCES**

- The Exam > **2018 Chief Reader Report**

LEARNING OBJECTIVE**9.9.A**

Explain whether an electrochemical cell is thermodynamically favored, based on its standard cell potential and the constituent half-reactions within the cell.

ESSENTIAL KNOWLEDGE**9.9.A.1**

Electrochemistry encompasses the study of redox reactions that occur within electrochemical cells. The reactions are either thermodynamically favored (resulting in a positive voltage) or thermodynamically unfavored (resulting in a negative voltage and requiring an externally applied potential for the reaction to proceed).

9.9.A.2

The standard cell potential of electrochemical cells can be calculated by identifying the oxidation and reduction half-reactions and their respective standard reduction potentials.

9.9.A.3

ΔG° (standard Gibbs free energy change) is proportional to the negative of the cell potential for the redox reaction from which it is constructed. Thus, a cell with a positive E° involves a thermodynamically favored reaction, and a cell with a negative E° involves a thermodynamically unfavored reaction.

$$\text{EQN: } \Delta G^\circ = -nFE^\circ$$

SUGGESTED SKILL

 Argumentation**6.D**

Provide reasoning to justify a claim using chemical principles or laws, or using mathematical justification.



AVAILABLE RESOURCES

- The Exam > [2022 Chief Reader Report](#)

TOPIC 9.10

Cell Potential Under Nonstandard Conditions

Required Course Content

LEARNING OBJECTIVE**9.10.A**

Explain the relationship between deviations from standard cell conditions and changes in the cell potential.

ESSENTIAL KNOWLEDGE**9.10.A.1**

In a real system under nonstandard conditions, the cell potential will vary depending on the concentrations of the active species. The cell potential is a driving force toward equilibrium; the farther the reaction is from equilibrium, the greater the magnitude of the cell potential.

9.10.A.2

Equilibrium arguments such as Le Châtelier's principle do not apply to electrochemical systems, because the systems are not in equilibrium.

9.10.A.3

The standard cell potential E° corresponds to the standard conditions of $Q = 1$. As the system approaches equilibrium, the magnitude (i.e., absolute value) of the cell potential decreases, reaching zero at equilibrium (when $Q = K$). Deviations from standard conditions that take the cell further from equilibrium than $Q = 1$ will increase the magnitude of the cell potential relative to E° . Deviations from standard conditions that take the cell closer to equilibrium than $Q = 1$ will decrease the magnitude of the cell potential relative to E° . In concentration cells, the direction of spontaneous electron flow can be determined by considering the direction needed to reach equilibrium.

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LEARNING OBJECTIVE

9.10.A

Explain the relationship between deviations from standard cell conditions and changes in the cell potential.

ESSENTIAL KNOWLEDGE

9.10.A.4

Algorithmic calculations using the Nernst equation are insufficient to demonstrate an understanding of electrochemical cells under nonstandard conditions. However, students should qualitatively understand the effects of concentration on cell potential and use conceptual reasoning, including the qualitative use of the Nernst equation:

EQN: $E = E^\circ - (RT/nF) \ln Q$
to solve problems.

SUGGESTED SKILL *Mathematical Routines***5.B**

Identify an appropriate theory, definition, or mathematical relationship to solve a problem.

TOPIC 9.11

Electrolysis and Faraday's Law

Required Course Content

LEARNING OBJECTIVE**9.11.A**

Calculate the amount of charge flow based on changes in the amounts of reactants and products in an electrochemical cell.

ESSENTIAL KNOWLEDGE**9.11.A.1**

Faraday's laws can be used to determine the stoichiometry of the redox reaction occurring in an electrochemical cell with respect to the following:

- i. Number of electrons transferred
- ii. Mass of material deposited on or removed from an electrode (as in electroplating)
- iii. Current
- iv. Time elapsed
- v. Charge of ionic species

EQN: $I = q/t$