

Applications of Thermodynamics

9.1 Introduction to Entropy

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.

Relative low ΔS° | $s < l < g$ | relative high ΔS°

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 the gas-phase products is greater than the total number of moles of gas-phase reactants.

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.

9.2 Absolute Entropy and Entropy Change

The entropy change for a process can be calculated from the absolute entropies of the species involved before and after the process occurs. It is often measured in joules. Every substance has a nonzero value for absolute entropy. The number of moles for each substance (from the balanced equation) must be considered when calculating entropy.

$$\Delta S^\circ_{\text{reaction}} = \sum S^\circ_{\text{products}} - \sum S^\circ_{\text{reactants}}$$

9.3 Gibbs Free Energy and Thermodynamic Favorability

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, such 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° .

The standard Gibbs free energy change for a chemical or physical process is a measure of the thermodynamic favorability. Historically, the term “spontaneous” has been used to describe the process 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.

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.

$$\Delta G_{\text{reaction}}^\circ = \sum \Delta G_{f \text{ products}}^\circ - \Delta G_{f \text{ reactants}}^\circ$$

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.

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

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

In general, the temperature conditions for a process to be thermodynamically favored (ΔG°) can be predicted from the signs below 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 ($\Delta G^\circ > 0$).

9.4 Thermodynamic and Kinetic Control

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

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 a process is under kinetic control.

9.5 Free Energy and Equilibrium

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

The equilibrium constant is related to free energy by the equations

$$K = e^{\frac{-\Delta G^\circ}{RT}}$$

and

$$\Delta G^\circ = -RT \ln K$$

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

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

9.6 Coupled Reactions

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

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

A desired product can be formed by coupling a thermodynamically favored reaction that produces what 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. Hess's law is applied and the sum of the individual reactions produces an overall reaction that achieves the desired outcome and the $\Delta G^\circ < 0$.

9.7 Galvanic (Voltaic) and Electrolytic Cells

An electrochemical cell is a device that can convert energy released by a thermodynamically favored redox reaction to electrical energy to drive a thermodynamically unfavored redox reaction. Each component of an electrochemical cell (electrodes, solutions in half-cells, salt bridge, voltage/current measuring device) plays a specific role in the overall functioning of the cell. The operation 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.

Galvanic, sometimes called voltaic, cells involve a thermodynamically favored reaction, whereas electrolytic cells involve a thermodynamically unfavored reaction. They both contain an anode (where oxidation occurs) and a cathode (where reduction occurs). Visual representations of galvanic and electrolytic cells are tools of analysis to identify where half-reactions occur and in what direction current flows.

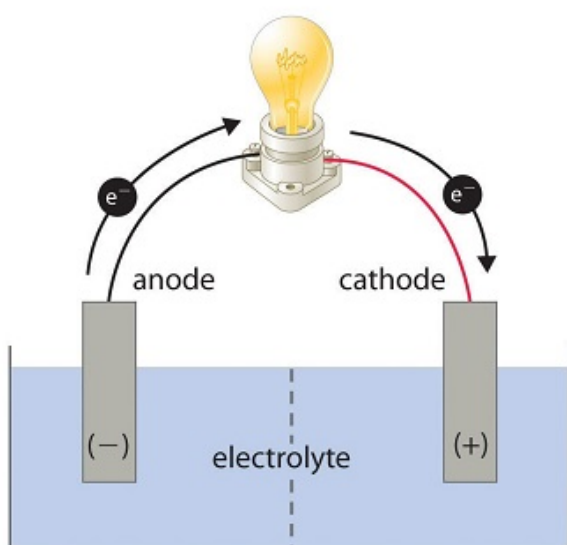
For all electrochemical cells, oxidation occurs at the anode and reduction occurs at the cathode.

Will not be assessed on labeling and electrode as positive or negative.

GALVANIC	ELECTROLYTIC
Thermodynamically favorable reaction	Thermodynamically unfavorable reaction
Anode and cathode in separate chambers (half-cells)	Anode and cathode in the same chamber
Salt bridge needed	No salt bridge needed
No power source needed	Power source needed
Produces electrical energy (positive voltage value)	Uses electrical energy (negative voltage value)
BOTH TYPES OF CELLS	
Oxidation at anode, reduction at cathode	

BOTH TYPES OF CELLS

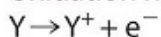
Require ion flow in the cell for reaction to occur (cations \rightarrow cathode; anions \rightarrow anode)



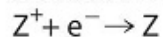
GALVANIC CELL

Energy released by spontaneous redox reaction is converted to electrical energy.

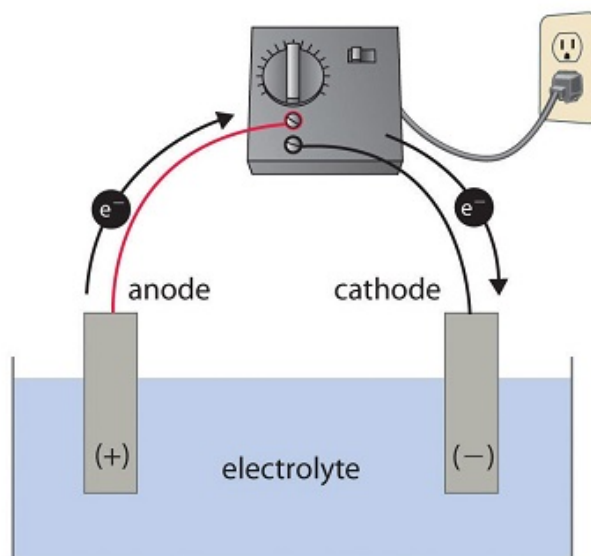
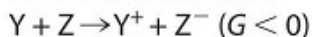
Oxidation half-reaction:



Reduction half-reaction:



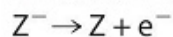
Overall cell reaction:



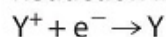
ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

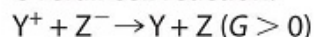
Oxidation half-reaction:



Reduction half-reaction:



Overall cell reaction:



9.8 Cell Potential and Free Energy

A reaction occurring in an electrochemical cell involves an electric potential difference (voltage) between the oxidation and reduction processes occurring in half-cells. The symbol for reduction potential is E and the units are volts (V). For purposes of comparing the reduction potentials of different oxidation and reduction processes, standard reduction potentials (E_{red}°) are used. These potentials are only accurate under standard conditions. Electrical potential does not depend on the amount of substance reacting. Do not multiple the values of the half-reaction potentials by the coefficients in the overall cell reaction.

$$E_{cell}^\circ = E_{cathode}^\circ - E_{anode}^\circ$$

The minus sign accounts for the reversal of the reduction potential for this process.

The cathode E° is positive and the anode E° is negative.

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 disfavored (resulting in a negative voltage and requiring an externally applied potential for the reaction to proceed).

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

A cell with a positive E° involves a thermodynamically favored reaction, and a cell with a negative E° involves a thermodynamically disfavored reaction.

ΔG° (standard Gibbs free energy change) is proportional to:

- The negative of the cell potential for the redox reaction from which it is constructed
- The moles of the electrons (n) transferred in the redox reaction
- Faraday's constant, F (the amount of charge (q), in coulombs (C), per mole of electrons)

- $F = 96,485 \frac{C}{mol\ e^-}$

$$\Delta G^\circ = -nFE^\circ$$

9.9 Cell Potential Under Nonstandard Conditions

NEED MORE HELP

In a real system under nonstandard conditions, the cell potential depends 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 cell potential.

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

The standard cell potential E° corresponds to the standard condition $Q = 1$. As the system approaches equilibrium, the magnitude (i.e., absolute value) of the cell potential decreases, reaching zero at equilibrium (where $Q = K$). In a voltaic cell, $K > 1$. Thus, when Q is increased above 1, the system moved closer to equilibrium and the cell potential decreases relative to standard conditions. Conversely, when Q decreases below 1, the cell is further from equilibrium and cell potential increases relative to standard conditions. The opposite effects are observed in electrolytic cells, because $K < 1$. Note

that “increasing the magnitude” of the cell potential in electrolytic cells means making it more negative. E° . In concentration cells, the directions of spontaneous electron flow can be determined by considering the direction needed to reach equilibrium.

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 the conceptual reading, including the qualitative use of the Nernst equation:

$$E = E^\circ - \left(\frac{RT}{nF}\right) \ln Q$$

to solve problems.

Summary

In a voltaic cell, increasing Q means decreasing E_{cell} , and decreasing Q means increasing E_{cell} . The opposite relationship can be seen in electrolytic cells (but remember that this refers to $|E_{cell}|$ because cell potentials are negative). Changing the mass of solids does not affect cell potential because solids are not in the Q expression.

9.10 Electrolysis and Faraday’s Law

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

- Number of electrons transferred
- Mass of material deposited on or removed from an electrode
- Current
- Time elapsed
- Charge of ionic species

$$q = I \times t$$

$I = \text{current (A = } \frac{\text{C}}{\text{s}} \text{)}$

$q = \text{amount of charge (C)}$

$t = \text{time (s)}$

A “faraday” is a mole of electrons