AP CHEM

Chapter 5 Outline

Pressure

- A gas uniformly fills any container, is easily compressed and mixes completely with any other gas.
- The barometer (shown to the right) was invented in 1643 by Evangelista Torricelli (a student of Galileo). A barometer is constructed by filling a glass tube with mercury and inverting it in a dish of mercury. The atmospheric pressure keeps the mercury in the tube. At sea level, the column of mercury is 760 mm.
- Atmospheric pressure changes with the weather. A low pressure system usually brings a storm. Atmospheric pressure also changes with altitude. At higher altitudes, there is less air and thus less atmospheric pressure.
- A manometer (shown below) is used to measure pressure of a gas in a container.



The Gas Laws of Boyle, Charles and Avogadro

- Boyle's Law
 - Boyle was the first to perform quantitative experiments on gases.
 - PV = k (k is a constant for a given sample of air at a specific temperature). Boyle's law is also represented as P₁V₁ = P₂V₂.
 There is an inverse relationship between pressure and volume. As pressure increase volume decreases. A plot of data shows a hyperbola. This can be seen to the right.
 - In the centuries since Boyle's original experiments, equipment and measuring techniques have improved and now it is evident that **Boyle's law only holds true at very low pressures**. At higher pressures, PV is not constant but varies as pressure is varied. A gas that strictly obeys Boyle's law is called an **ideal gas**.
 - **Example:** A 1.25 L sample of gaseous NO₂ is at a pressure of 5.4 x 10³ Pa. If the pressure is changed to 2.7 x 10⁴ Pa at a constant temperature, what will be the new volume of the gas? $P_1V_1 = P_2V_2$

$$(5.4 \times 10^3) (1.25) = (2.7 \times 10^4) X$$

X = 0.25 L



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- Mercury is used in barometers and manometers because of its density.
 A column of water would be 13.5 times as high as a column of mercury.
- Standard atmospheric pressure: 1 atm = 760 mm Hg = 760 torr = 14.70 psi = 101325 Pa
- The SI Unit for pressure is the pascal (Pa).



Always make sure the answer makes sense. Since the pressure increases, the volume should decrease.

• You try one: An aerosol can contains 400. mL of a compressed gas at 5.20 atm pressure. When all of the gas is sprayed into a large plastic bag, the bag inflates to a volume of 2.14 L. What is the pressure of the gas inside the plastic bag. Assume temperature is constant.

Charles's law

- o Jacques Charles was the first to fill a balloon with hydrogen gas and make a solo balloon flight.
- Charles found that the volume of a gas at constant pressure increases linearly with the temperature of the gas.
- The volume of a gas is directly proportional to temperature and extrapolates to zero when temperature is 0 K.
- V= bT; V = volume, T = temperature in Kelvin and b is the proportionality constant. Charles's law is often used as: $V_1/T_1 = V_2/T_2$
- Example: A gas at a temperature of 20.°C and 1 atm has a volume of 2.58 L. What volume will it occupy at 35.°C and 1 atm? $V_1/T_1 = V_2/T_2$

Temperature must be in Kelvin. $T_1 = 20. + 273 = 293$ K

$$T_2 = 35 + 273 = 308 \text{ k}$$



2.58/293 = X/308

X = 2.71 L

Always make sure the answer makes sense. Since the temperature increases, the volume should increase.

• You try one: A balloon is filled to a volume of 7.00×10^2 mL at a temperature of 20.0° C. The balloon is then cooled at constant pressure to a temperature of 1.00×10^2 K. What is the final volume of the balloon?

Avogadro's Law

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- Avogadro postulated that equal volumes of gases at the same temperature and pressure contain the same number of "particles"
 - V = an; V = volume, n = number of moles, a = proportionality constant; also written as: $V_1/n_1 = V_2/n_2$
- For a gas at a constant temperature and pressure, the volume is directly proportional to the number of moles of gas.
- Example: A 15.5 L sample containing 0.40 moles of oxygen gas (O_2) at a pressure of 1 atm and a temperature of 25°C. If all of the O_2 is converted to ozone (O_3) at the same pressure and temperature, calculate the volume of ozone (O_3) .

$$3O_2 \rightarrow 2O_3$$

0.40 moles O_2 x 2 moles of O_3 = 0.27 moles O_3
1 3 moles of O_2
15.5/0.40 = X/0.27
X = 10. L

• You try one: Consider the following equation:

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2NO_2(g) \rightarrow N_2O_4(g)
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If 25.0 mL of NO_2 gas is completely converted to N_2O_4 gas under the same conditions, what volume will the N_2O_4 occupy?

The Ideal Gas Law

- When the previous three laws are combined, the ideal gas law is formed: PV = nRT; P = pressure, V = volume, n = number of moles, R= ideal gas law constant (0.08206 L atm/mol K), T = temperature (in Kelvin)
- The ideal gas law is a limiting law it expresses behavior that real gases approach at low pressures and high temperatures.
- Ideal gases are hypothetical substances; though most gases obey the ideal gas law equation closely enough at pressures below 1 atm.
- Example: A sample of oxygen gas (O₂) has a volume of 8.48 L at a temperature of 20.°C and a pressure of 1.2 atm. Calculate the moles of O₂ molecules present in the gas sample.
 PV = nRT

(1.2)(8.48) = n (0.08206)(293)

n = 0.42 moles

• You try one: What is the volume of 2.00 moles of an ideal gas at a pressure of 5.00 atm and a temperature of 155°C?

An important use of the ideal gas law is to determine the molar mass of a gas from its measured density. By manipulating the ideal gas law formula you can come up with: Molar Mass = dRT/P; d = density, R = ideal gas law constant, P = pressure

• **Example:** A gas has a density of 1.87 g/L at a pressure of 1.60 atm and 23°C. Calculate the molar mass of the gas.

Molar Mass = dRT/P MM = (1.87)(0.08206)(296)/(1.60) MM = 28.4 g/mol

• You try one: A gas has a density of 2.49 g/L at a pressure of 1.12 atm and 40.°C. Calculate the molar mass of the gas.

Gas Stoichiometry

- 1 mole of an ideal gas has a volume of 22.42 L at 0°C and 1 atm
- 0°C and 1 atm are referred to as standard temperature and pressure (STP)
- Example: Calculate the volume of CO₂ produced in the combustion of 20.0 grams of ethane at STP. $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$ $20.0 \text{ g } C_2H_6 \text{ x } 1 \text{ mole } C_2H_6 \text{ x } 4 \text{ moles } CO_2 \text{ x } 22.42 \text{ L } CO_2 = 29.8 \text{ L } CO_2$ $1 \quad 30.068 \text{ g } C_2H_6 \text{ 2 moles } C_2H_6 \quad 1 \text{ mole } CO_2$
- You try: Calculate the volume of hydrogen gas produced when 35.0 grams of zinc are reacted with excess hydrochloric acid at STP.

 $Zn(s) + 2HCl(aq) \rightarrow ZnCl_2(aq) + H_2(g)$

Dalton's Law of Partial Pressure

- Among the experiments that led John Dalton to propose his atomic theory were his studies of mixtures of gases.
- In 1803 Dalton proposed that for a mixture of gases in a container, the total pressure exerted is a sum of the pressure that each gas would exert if it were alone.
 Assuming each gas to behave ideally, the partial pressure of each gas can be: P₁ = n₁RT/V, P₂ = n₂RT/V, etc.
- The total pressure of a mixture can be represented as $P_{total} = P_1 + P_2 + P_3$...etc
- **Example:** Mixture of helium and oxygen can be used in scuba diving tanks to help prevent "the bends". For a particular dive, 46 L He at 25°C and 1.0 atm and 12 L O₂ at 25°C and 1.0 atm were pumped into a tank with a volume of 5.0 L. Calculate the partial pressure of each gas and the total pressure at 25°C. $P_{He} = n_{He}RT/V$

 $r_{He} = n_{He} R1/v$ $1.0 = n_{He} (0.08206)(298)/(46)$ $n_{He} = 1.9 \text{ mol}$

 $P_{O2} = n_{O2}RT/V$ 1.0 = $n_{O2}(0.08206)(298)/(12)$ $n_{O2} = 0.49 \text{ mol}$

The tank has a volume of 5.0 L and the temperature is 25°C. Use the ideal gas law to calculate the pressure of each gas.

 $P_{He} = n_{He}RT/V$ $P_{He} = (1.9)(0.082060)(298)/5.0$ $P_{He} = 9.3$ atm

$$\begin{split} P_{O2} &= n_{O2} R T/V \\ P_{O2} &= (0.49)(0.082060)(298)/5.0 \\ P_{O2} &= 2.4 \text{ atm} \end{split}$$

$$\begin{split} \mathbf{P}_{total} &= \mathbf{P}_{He} + \mathbf{P}_{O2} \\ \mathbf{P}_{total} &= 9.3 + 2.4 \\ \mathbf{P}_{total} &= 11.7 \text{ atm} \end{split}$$

• You try one: A mixture of 1.00 g H₂ and 1.00 g He is placed in a 1.00 L container at 27°C. Calculate the partial pressure of each gas and the total pressure.

- Mole fraction: the ratio of the number of moles of a given component in a mixture to the total number of • moles in the mixture.
- The formula used in determining mole fractions is: $X_1 = n_1/n_{total} = P_1/P_{total}$ (use either moles or pressure). Mole fraction has no units.
- **Example:** The partial pressure of oxygen was observed to be 156 torr in air with a total atmospheric pressure of 743 torr. Calculate the mole fraction of O_2 present.
 - $X_1 = P_1 / P_{total}$
 - $X_1 = 156/743$ $X_1 = 0.210$
- You try one: The partial pressure of $CH_4(g)$ is 0.175 atm and that of $O_2(g)$ is 0.250 atm in a mixture of the two gases. Calculate the mole fraction of each gas in the mixture.

Dalton's law is also applicable when it comes to gas collection over water. A mixture of gases results whenever a gas is collected by

displacement of water. Observe the diagram below: Oxygen gas is produced through the decomposition of potassium chlorate. The gas in the bottle is a mixture of oxygen and water vapor. Water vapor is present because water molecules escape from the surface of the liquid and collect in the space above the liquid. When the rate of evaporation equals the rate of



condensation, equilibrium is reached. The pressure exerted by the water vapor depends on temperature and is referred to as the vapor pressure of water.

Example: A sample of solid potassium chlorate (KClO₃) was heated in a test tube and decomposed by the following reaction: $2KClO_3 \rightarrow 2KCl + 3O_2$

The oxygen produced was collected by displacement method at 22°C at a total pressure of 754 torr. The volume of the gas collected was 0.650 L and the vapor pressure of water at 22°C is 21 torr. Calculate the partial pressure of O₂ in the gas collected and the mass of KClO₃ in the sample that was decomposed.

$$P_{\text{total}} = P_{02} + P_{\text{H2O}}$$

$$754 = X + 21$$

$$X = 733 \text{ torr}$$
Convert torr to atm:
$$\frac{733 \text{ torr}}{1} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.964 \text{ atm}$$
Plug in to the ideal gas law equation to find the moles of oxygen gas:
$$P_{02} = n_{02} \text{RT/V}$$

$$0.964 = n_{02}(0.08206)(295)/(0.650)$$

$$n_{02} = 2.59 \times 10^{-2} \text{ mol}$$
Use stoichiometry to solve for mass of KCIO₃

$$\frac{2.59 \times 10^{-2} \text{ mol O}_2}{1} \times \frac{2 \text{ mol KCIO}_3}{3 \text{ mol O}_2} \times \frac{122.6 \text{ g KCIO}_3}{1 \text{ mole KCIO}_3} = 2.12 \text{ g KCIO}_3$$

• You try one: Helium is collected over water at 25°C and 1.00 atm total pressure. What volume of the gas must be collected to obtain 0.586 g helium? (At 25°C the vapor pressure of water is 23.8 torr.)

The Kinetic Molecular Theory of Gases

- The Kinetic Molecular Theory (KMT) is a model that attempts to explain the properties of an ideal gas.
- Note that models can never be proved absolutely true. Instead models are used to predict approximate behavior and more complicated models to account very precisely for observed quantitative data.
- The KMT states:
 - The particles of an ideal gas are so small compared with the distances between them that the volume of individual particles can be assumed to be negligible (zero).
 - The particles of an ideal gas are in constant motion. The collisions of the particles with the walls of the container are the cause of the pressure exerted by the gas.
 - The particles of an ideal gas are assumed to exert no forces on each other; no attraction or repulsion between particles.
 - The average kinetic energy of gas particles of an ideal gas is assumed to be directly proportional to the Kelvin temperature of the gas.

• Root Mean Square Velocity

- Root mean square velocity, $v_{rms} = \sqrt{3RT/M}$ R = 8.3145 J/mol K, T = temperature, M = mass of a mole in kilograms, also important : J = Kg m²/s²
- The average distance a particle travels between collisions in a particular gas sample is called the mean free path. It is typically a very small distance (1×10^{-7} m for O₂ at STP).
- **Example:** Calculate the root mean square velocity for the atoms in a sample of helium at 25°C. $M = 4.00 \text{ grams} \times 1 \text{ kilogram} = 4.00 \times 10^{-3} \text{ kg/mole}$

mole 1000 grams

$$T = 25 + 273 = 298 \text{ K}$$

 $v_{rms} = \sqrt{3RT/M}$
 $v_{rms} = \sqrt{3(8.3145 \text{ J/mol K})(298 \text{ K})/4.00 \text{ x } 10^{-3} \text{ kg/mol}}$
 $v_{rms} = \sqrt{1.86 \text{ x } 10^6 \text{ m}^2/\text{s}^2}$
 $v_{rms} = 1.36 \text{ x } 10^3 \text{ m/s}$

You try: Calculate the root mean square velocity for the atoms in a sample of oxygen gas at 20.°C

Effusion and Diffusion

- Diffusion is used to describe the mixing of gases. The rate of diffusion is the rate at which gases mix.
- Effusion is used to describe the passage of a gas through a tiny orifice into an evacuated chamber.
 - Thomas Graham (1805-1869), a Scottish chemist, found experimentally that the rate of effusion of a gas is inversely proportional to the square root of the mass of its particles.

0	Graham's law of effusion:	<u>Rate₁ = $\sqrt{\text{molar mass }_2}$</u>
		Rate ₂ $\sqrt{\text{molar mass}}_1$
0	For diffusion, the law would be:	<u>Distance traveled_1</u> = $\sqrt{\text{molar mass }_2}$
		Distance traveled ₂ $\sqrt{\text{molar mass }_1}$

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• **Example:** Calculate the ratio of the effusion of hydrogen and nitrogen gases. $\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{\sqrt{\text{molar mass }_2}}{\sqrt{\text{molar mass }_1}}$

 $\frac{\text{Rate}_{\text{H2}}}{\text{Rate}_{\text{N2}}} = \frac{\sqrt{28.0}}{\sqrt{2.0}} = 3.7$ The rate of effusion of hydrogen is 3.7 times faster than the effusion of nitrogen.

- You try: If it takes a sample of neon gas 45 seconds to completely effuse, how long would it take an equal volume of xenon to effuse.
- Try another: If nitrogen molecules effuse at a rate of 550 m/s, what would the rate of effusion hydrogen molecules be?

Real Gases

- An ideal gas is a hypothetical concept. No gas exactly follows the ideal gas law, although many gases come very close at low pressures and/or high temperatures. The ideal gas behavior can best be thought of as the behavior approached by real gases under certain conditions.
- In 1837 Johannes van der Waals (1837 1923) modified the ideal gas law to make it applicable to real gases. Van der Waals made adjustments to volume to account for the fact that real gases have finite volumes and he made adjustments to the pressure to account for the fact that real gases have attractions between molecules.
- $[P_{obs} + a(n/V)^2] \times (V nb) = nRT$
- You try: Calculate the pressure of 2.00 moles of oxygen in a 5.00 liter container at 298 K using the van der Waals equation

Chemistry in the Atmosphere

- The principle components of the atmosphere are nitrogen (78.08%) and oxygen (20.95%) but also includes numerous other gases in small amounts.
- Heavier molecules are found near the earth's surface and lighter gases are found higher in the atmosphere.
- The lowest layer of the atmosphere is called the troposphere.
- The chemistry occurring in the upper atmosphere is mostly determined by the effects of high-energy radiation and particles from the sun and other sources in space. The ozone in the upper atmosphere prevents high-energy ultraviolet radiation from reaching the earth.
- The chemistry occurring in the troposphere is influenced by human activity. Severe air pollution is apparent in most cities. Two sources of this air pollution are transportation and the production of electricity.

TABLE 5.3

Values of the van der Waals Constants for Some Common Gases

Gas	$a\!\left(\!\frac{atm\cdot L^2}{mol^2}\!\right)$	$b\left(\frac{L}{mol}\right)$
He	0.0341	0.0237
Ne	0.211	0.0171
Ar	1.35	0.0322
Kr	2.32	0.0398
Xe	4.19	0.0511
H ₂	0.244	0.0266
N ₂	1.39	0.0391
0,	1.36	0.0318
Cl ₂	6.49	0.0562
CO,	3.59	0.0427
CH4	2.25	0.0428
NH ₃	4.17	0.0371
H ₂ O	5.46	0.0305

- Combustion of petroleum in vehicles produces CO, CO₂, NO & NO₂.
- The chemistry of air pollution focuses primarily on the nitrogen oxides (NO_x). At high temperatures in vehicle engines, nitrogen reacts with oxygen to form nitrogen monoxide.

$$N_2 + O_2 \rightarrow 2NO$$

- Nitrogen monoxide is immediately oxidized in air to form nitrogen dioxide.
 - \circ 2NO + O₂ \rightarrow 2NO₂
- Nitrogen dioxide absorbs energy from sunlight and breaks into nitric oxide and free oxygen atoms
 NO₂ → NO + O
- Free oxygen atoms react with oxygen molecules to form ozone.

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\circ \quad O + O_2 \rightarrow O_3
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- Ozone is very reactive and can react directly with other pollutants, or ozone can absorb light and break up to form an energetically excited oxygen molecule (O₂^{*}) and an energetically excited oxygen atom (O^{*}).
 O₃ → O₂^{*} + O^{*}
- The energetically excited oxygen atom reacts with water to form 2 hydroxyl radicals.
 O^{*} + H₂O → 2OH
- The hydroxyl radical is a very reactive oxidizing agent and can react with nitrogen dioxide to form nitric acid.
 - $\circ \quad OH + NO_2 \rightarrow HNO_3$
- The hydroxyl radical can also react with the unburned hydrocarbons in the polluted air to produce chemicals that cause the eyes to water or burn and are harmful to the respiratory system.
- The end result of this process is call photochemical smog because light is required to initiate some of the reactions.
- Attempts to reduce photochemical smog are focused on cutting down the amounts of molecules from unburned fuel in automobile exhaust and designing engines that produce less nitric oxide.
- Another source of pollution is in the production of electricity.
- Much of the coal found in the Midwest contains sulfur which when burned produces sulfur dioxide.
 S (from coal) + O₂ → SO₂
- Sulfur dioxide is changed to sulfur trioxide in air. This is generally a slow process, unless solid particles are present.

 \circ 2SO₂ + O₂ \rightarrow 2SO₃

- Sulfur trioxide reacts with water vapor to form sulfuric acid.
 - $\circ \quad SO_3 + H_2O \rightarrow H_2SO_4$
- This type of pollution leads to acid rain.
- One way to use coal without harming the air quality is to remove the sulfur dioxide from the exhaust gas by means of a system called a scrubber before it is emitted from the power plant stack. A common method of scrubbing is to blow powdered limestone (CaCO₃) into the combustion chamber where it decomposes into lime (CaO) and carbon dioxide (CO₂).
 - $\circ \quad CaCO_3 \rightarrow CaO + CO_2$
- The lime reacts with sulfur dioxide to form calcium sulfite.
 - $\circ \quad CaO + SO_2 \rightarrow CaSO_3$
- Unfortunately there are many problems associated with scrubbing. The systems are complicated and expensive and consume a great deal of energy. Plus the large quantities of calcium sulfite produced, creates a disposal problem. A typical scrubber produces 1 ton of calcium sulfite per year for each person the power plant serves.





Gas Law Formulas		
$\mathbf{P}_{\text{total}} = \mathbf{P}_1 + \mathbf{P}_2 + \mathbf{P}_3$	Dalton's Law of Partial Pressure	
$X_i = n_i/n_{total} = P_i/P_{total}$	Mole Fraction	
$\mathbf{P}_{1}\mathbf{V}_{1}=\mathbf{P}_{2}\mathbf{V}_{2}$	Boyle's Law	
$\mathbf{V}_{1}/\mathbf{T}_{1}=\mathbf{V}_{2}/\mathbf{T}_{2}$	Charles' Law	
$\mathbf{V}_{1}/\mathbf{n}_{1}=\mathbf{V}_{2}/\mathbf{n}_{2}$	Avogadro's Law	
$\mathbf{P}_{1}/\mathbf{T}_{1}=\mathbf{P}_{2}/\mathbf{T}_{2}$	Gay-Lussac's Law	
$\mathbf{P}_{1}\mathbf{V}_{1} / \mathbf{T}_{1} = \mathbf{P}_{2}\mathbf{V}_{2} / \mathbf{T}_{2}$	Combined Gas Law	
$\frac{\text{Rate}_{B}}{\text{Rate}_{A}} = \frac{-\sqrt{MM_{A}}}{-\sqrt{MM_{B}}}$	Graham's Law	
PV = nRT R = 8.3145 L kPa/mol K or R= 0.08206 L atm/mol K	Ideal Gas Law	
(mm) P = dRT mm = molar mass d = density R= 0.08206 L atm/mol K	Gas Density/Molar Mass	
$v_{rms} = \sqrt{(3RT / M)}$ M = molar mass in kg / mol R = 8.3145 J/mol K	Root Mean Square Velocity	
$[P_{obs} + a(n/V)^2] x (V - nb) = nRT$	van der Waals Equation	
Standard Atmospheric Pressure: 1 atm = 760 torr = 760 mm Hg = 101.3 kPa = 14.7 psi		

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The formulas used in this chapter are listed below:

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$$PV = nRT$$

$$\left(P + \frac{n^{2}a}{V^{2}}\right)(V - nb) = nRT$$

$$P_{A} = P_{total} \times X_{A}, \text{where } X_{A} = \frac{\text{moles } A}{\text{total moles}}$$

$$P_{total} = P_{A} + P_{B} + P_{C} + \dots$$

$$n = \frac{m}{M}$$

$$K = ^{\circ}C + 273$$

$$\frac{P_{1}V_{1}}{T_{1}} = \frac{P_{2}V_{2}}{T_{2}}$$

$$D = \frac{m}{V}$$

$$u_{rms} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

$$KE \text{ per molecule} = \frac{1}{2}mv^{2}$$

$$KE \text{ per mole} = \frac{3}{2}RT$$

$$\frac{r_{1}}{r_{2}} = \sqrt{\frac{M_{2}}{M_{1}}}$$

$$molarity, M = \text{ moles solute per liter solution}$$

$$molarity = moles solute per kilogram solvent$$

$$\Delta T_{f} = iK_{f} \times \text{molality}$$

$$\pi = iMRT$$

$$A = abc$$

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$$P = \text{pressure}$$

$$V = \text{volume}$$

$$T = \text{temperature}$$

$$n = \text{number of moles}$$

$$D = \text{density}$$

$$m = \text{mass}$$

$$v = \text{velocity}$$

$$u_{rms} = \text{root-mean-square speed}$$

$$KE = \text{kinetic energy}$$

$$r = \text{rate of effusion}$$

$$M = \text{molar mass}$$

$$\pi = \text{osmotic pressure}$$

$$i = \text{van't Hoff factor}$$

$$K_f = \text{molal freezing-point depression constant}$$

$$A = \text{absorbance}$$

$$a = \text{molar absorptivity}$$

$$b = \text{path length}$$

$$c = \text{concentration}$$

$$Q = \text{reaction quotient}$$

$$I = \text{current (amperes)}$$

$$q = \text{charge (coulombs)}$$

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

- $E^{\circ} =$ standard reduction potential
- K = equilibrium constant