AP Chemistry:
Study Guide

Key Exam Details

The AP® Chemistry exam is a 3-hour 15-minute, end-of-course test comprised of 60 multiple-choice questions, for which you will have 1 hour and 30 minutes (this counts for 50% of your score) and 7 free-response questions, for which you will have 1 hour and 45 minutes (this counts for 50% of your score).

The exam covers the following course content categories:

- Atomic Structure and Properties: 7–9% of test questions
- Molecular and Ionic Compound Structure and Properties: 7–9% of test questions
- Intermolecular Forces and Properties: 18–22% of test questions
- Chemical Reactions: 7–9% of test questions
- Kinetics: 7–9% of test questions
- Thermodynamics: 7–9% of test questions
- Equilibrium: 7–9% of test questions
- Acids and Bases: 11–15% of test questions
- Applications of Thermodynamics: 7–9% of test questions

This guide will offer an overview of the main tested subjects, along with sample AP multiple-choice questions that look like the questions you will see on test day.

Atomic Structure and Properties

Around 7–9% of questions on your AP Chemistry exam will cover Atomic Structure and Properties.

The physical world is made of **matter**, which is any substance that has mass and occupies space. **Atoms** are the fundamental unit of matter, and the smallest unit that retains all the properties of an element. **Molecules** are a group of atoms that are bonded together to form a chemical compound. This section will go into detail about the structure and properties of atoms.

Moles and Molar Mass

The international standard unit of measure for the number of molecules in a substance is a **mole**. A mole is equal to **Avogadro's number**, or 6.022×10^{23}, which is standardized to the number of atoms that are present in 12 grams of Carbon-12. A mole of a substance is always the same number of particles, regardless of what the substance is (e.g., hydrogen atoms, water particles, electrons). You can think of this in the same way that a dozen always means 12, regardless of whether it refers to eggs or days. The **molar mass** of substance, also called the **molecular weight** or **molecular mass**, is the total mass of one mole of that substance, expressed as grams/mole. Molar mass is used to convert the mass of a substance to the number of molecules present using the following conversion:

$$\text{\# of moles} = \frac{\text{weight in grams}}{\text{molar mass}}$$

# of moles of substance = (# of moles of substance) × (Avogadro's number)

This relationship is used to determine the number of molecules present given the mass of a pure chemical using the atomic mass on the periodic table. To determine the number of molecules present in a compound, calculate the number of moles present using mass in grams and the molar mass. This number is then multiplied by Avogadro's number to determine the number of molecules.

Mass Spectroscopy

Scientists can measure the abundance of different atoms in a sample using **mass spectroscopy**. A mass spectrometer separates molecules in a sample based on their charge and weight. To do this, the sample is first charged by bombarding it with electrons. Magnetic fields then separate ions by charge, and the relative abundance of ions in a sample are read by a detector. Ions of different masses need different strengths of magnetic fields to reach the detector. Results are plotted showing the mass-to-charge ratio on the *x*-axis (*m/z*) and the relative abundance of each atom type on the *y*-axis. You may be asked on the AP exam to determine the relative abundance of different isotopes of an element based on mass spec results.

Elemental Composition of Pure Substances

Pure substances are made of a single type of substance that has consistent characteristics and cannot be broken down further through physical processes. A pure substance that is made of a single type of atom is called an **element**. A pure substance that is made of only one type of molecule is called a **compound**. According to the **law of definite proportions**, a pure chemical compound broken down into elements always contains elements of a fixed ratio, independent of where and how it was created. For example, pure water will always contain the same ratio of hydrogen and oxygen, regardless of where it is found.

Composition of Mixtures

A **mixture** is made of more than one type of element or compound. The components in a mixture can have different proportions. For example, you can make a 20% saline solution out of 20% sodium chloride and 80% water, or you can make a 5% saline solution out of 5% sodium chloride and 95% water; yet both are still saline.

When you make a mixture, no chemical reactions take place, so you could still theoretically recover the individual components back to their pure forms. In the case of saline, you could evaporate off the water and recover both the sodium chloride and the water. Mixtures can be **homogenous**, meaning all parts of the mixture are identical to other parts due to even distribution of compounds, or mixtures can be **heterogenous**, as in there is a non-uniform distribution of compounds.

Atomic Structure and Electron Configuration

Atoms are made of smaller subatomic particles including positively charged **protons**, negatively charged **electrons**, and uncharged **neutrons**. Protons and neutrons together occupy the tightly packed nucleus of an atom, while electrons orbit outside of the nucleus in electron shells.

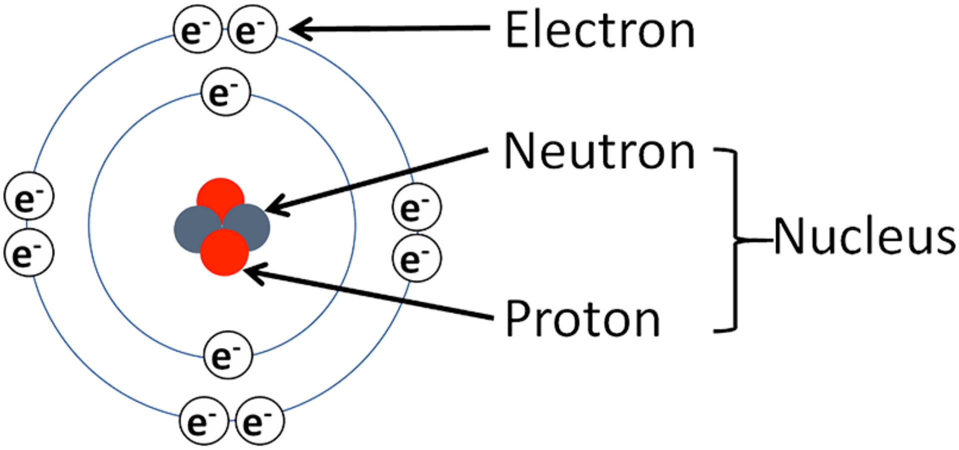
Together, subatomic particles determine the identity, mass, and charge of an atom. Protons and neutrons have the same approximate mass (1.67×10^{-27} kg), while electrons contribute a negligible amount of mass (roughly 1/1,800 the mass of the protons and neutrons). Thus, protons and neutrons are included in estimating mass of an element and electrons are not. The **mass number** is a whole number equal to the number of protons and neutrons of an element. The mass of a single proton or neutron is 1 **atomic mass unit** (amu). The number of protons in the nucleus is called the **atomic number.** The atomic symbol of an element is represented as:

$${}_{Z}^{A}X$$

Where X is the element symbol, A is the mass number, and Z is the atomic number. The atomic number defines which element an atom is. For example, carbon has 6 protons; the addition of a proton to a carbon atom would make it change to nitrogen. On the other hand, the number of neutrons in an individual atom of an element can vary, changing the mass number of an atom. Atoms with the same number of protons but different number of neutrons are called **isotopes** of an element. To determine the number of neutrons in an atom, subtract the atomic number from the mass number.

Atomic mass is the average mass number of all the atoms of that element. Atomic mass on the periodic table can give you an idea of the proportion of isotopes present. For example, lithium (L) has an atomic number of 3 and an atomic mass of 6.941, indicating that many lithium atoms on Earth have more than the 3 neutrons in their nucleus.

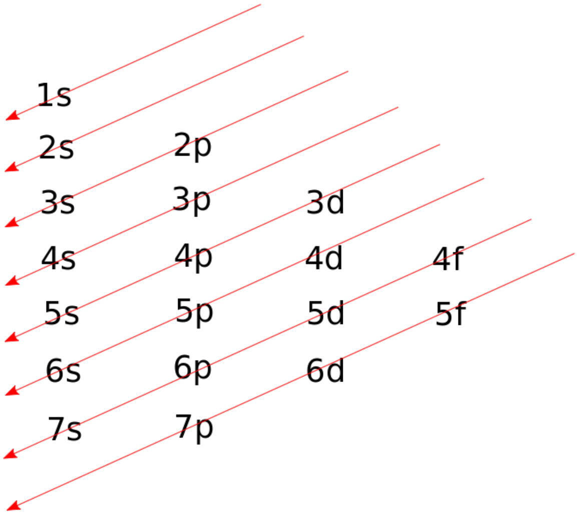
Atomic charge is determined by the relative number of electrons and protons of an atom. While the number of protons of an atom is stable, the number of electrons varies. Atoms with a non-zero charge are called **ions**. An atom with an equal number of protons and electrons has a neutral charge. Since electrons are negatively charged, the addition of an electron gives a negative charge to an atom, creating an **anion**. The loss of an electron gives a positive charge to an atom, which is called a **cation**.



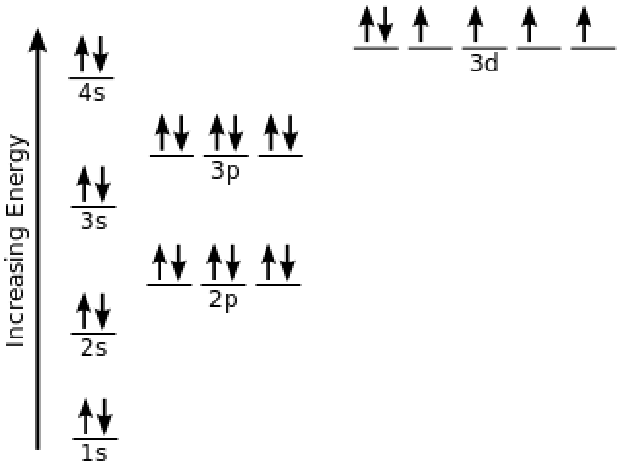
In current atomic models, electrons occupy space outside of the nucleus at discreet distances and energy levels called **shells**. The closer the shell is to the nucleus, the lower the relative energy level. Within each shell, there are **subshells** that have slightly different energy levels. Electron shells are numbered (n = 1, 2, 3 and so on), the number of the shell describes the number of subshells it holds. Subshells (l) are denoted by the letters and corresponding numbers: 0=*s*, 1=*p*, 2=*d*, 3=*f*, 4=*g*, 5=*h* in order of increasing energy and electron holding capacity. The space within a subshell that an electron has the highest probability of being is called an **orbital**. Each orbital can hold a maximum of two electrons.

You can calculate the number of electrons possible in a subshell or shell easily by using the shell number or the subshell letter. The number of orbitals in a subshell (l) is calculated by the equation $2l + 1$. In other words, subshell *d* has 5 possible orbitals ($2 \times 2 + 1=5$), and since each orbital can hold 2 electrons, *d* has an electron holding capacity of 10. Each shell has n^2 orbitals and can hold $2n^2$ electrons. For example, the first shell has 1 orbital (*s*) and can hold 2 electrons ($2 \times 1^2=2$) and the second shell has 4 orbitals (1 in *s* and 3 in *p*) and can hold 8 electrons ($2 \times 2^2=8$).

Electrons fill the lowest energy orbitals first. This is called the **Aufbau principle**. To figure out what shells fill first, follow the diagram showing the orbital diagonal rule. Remember that in some cases, orbitals in shells with a higher number can fill before those of a lower number; for instance, 4s has a lower energy than 3d, and will fill first. You may be asked on the exam to show the **electronic configuration** for an atom. In this notation, each subshell is written out in order of increasing energy and the number of electrons in each subshell is written in superscript. For example, neutral carbon has 6 electrons. The electronic configuration for this would be $1s^2 2s^2 2p^2$, meaning there are 2 electrons in subshell 1s, 2 electrons in subshell 2s, and 2 electrons in subshell 2p. To figure out the configuration on your own, you can follow the orbital diagram to map out which shells will be filled first.



According to **Hund's rule**, electrons fill all orbitals of equal energy with one electron before pairing electrons. That means that for carbon, the two electrons in the 2p subshell would not occupy the same orbital. To draw this out, you can represent each orbital in a subshell using the following diagram:



Here, each orbital is shown as a line and each electron for iron is shown as an arrow. You can fill in each electron for the atom in order of increasing energy. In the case of iron, the highest energy subshell 3d is not full and only has 6 of 10 possible electrons. Thus, according to Hund's rule, 4 of the 5 orbitals will have one electron and 1 orbital will have two electrons. The direction of an arrow in this diagram indicates the **spin** of an electron, either spin up or spin down. According to **Pauli's Exclusion Principle**, two electrons of the same spin cannot occupy the same orbital; thus, a single orbital can only have one spin up and one spin down electron.

When subshells are not filled, unpaired electrons are present and can interact with magnetic fields, making the atom **paramagnetic**. When all subshells are filled, the element does not interact with magnetic fields and is called **diamagnetic**. The outer shell is called the **valence shell**, which will be discussed in further detail.

The energy that is needed to remove an electron from an atom is called **ionization energy. Coulomb's law** is used to calculate ionization energy, or the energy needed to move an electron from one energy shell to another. According to Coulomb's law, the force of attraction or repulsion (*F*) between two charges is proportional to the product of charges (*Q*) divided by the square of the distance between them (*r*).

$$F = k\frac{Q_1Q_2}{r^2}$$

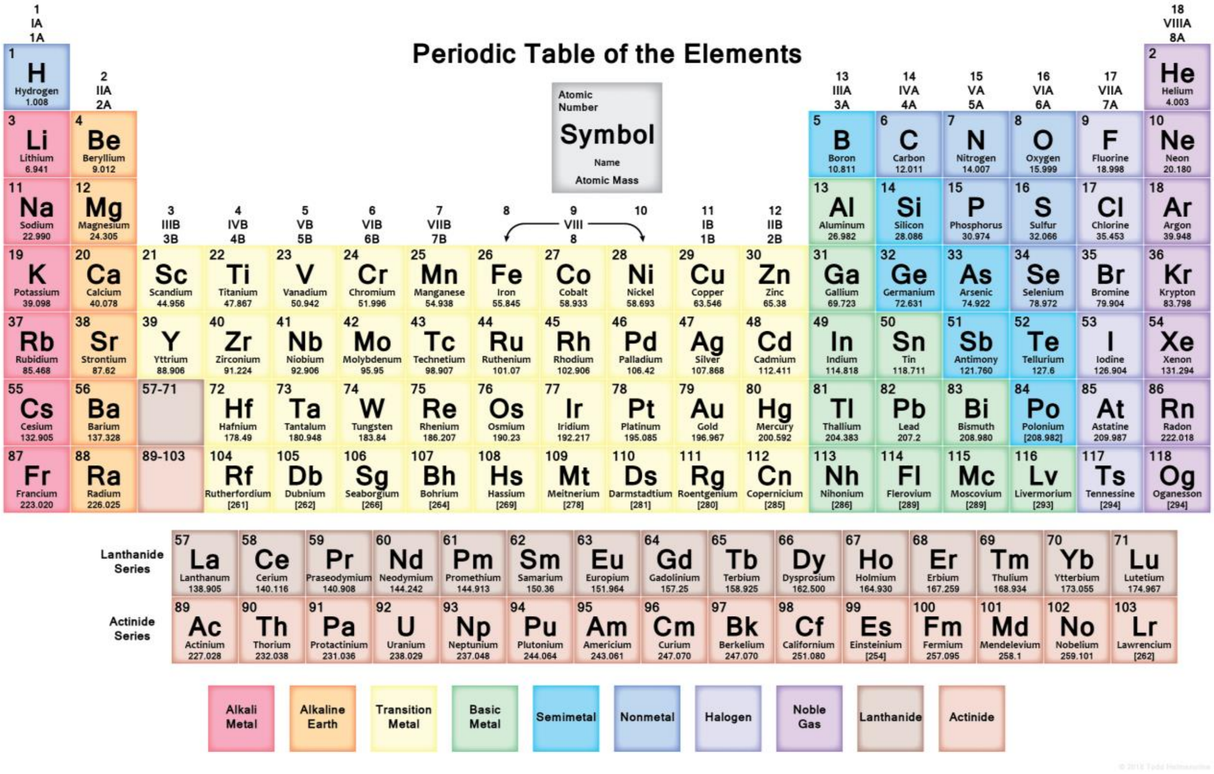
From this equation, you'll find that the attractive force between protons and electrons is highly dependent on their distance from the nucleus. In other words, it will take more energy to remove electrons that are closer to the nucleus than those that are farther away. Be prepared to use this calculation to estimate relative ionization energies on the AP exam.

Photoelectron Spectroscopy

Photoelectron spectroscopy (PES) is used to determine how many electrons an atom has and where they reside. This technique relies on ionization energy. In photoelectron microscopy, high energy radiation is focused onto a substance and the kinetic energy of electrons and relative abundance of electrons at each energy is detected. This information can be used to calculate an electron's **binding energy**, the energy needed to remove an electron from a subshell of an atom.

To remove an electron from an atom, the energy applied must be greater than the binding energy of the electron. The closer an electron is to the nucleus of an atom, the stronger the attraction to the nucleus; thus, electrons closer to the nucleus have greater binding energies. In a PES spectra, high energy peaks are made by electrons emitted from orbitals closer to the nucleus of the atom, and low energy peaks are made from electrons in or near the valance shell. The heights of the peaks can be used to calculate relative abundance, which is then used to determine the identity of an atom. In the free response exam section, you may be asked to identify elements and electron configurations based on PES spectra.

Periodic Trends



Periodic Table of the Elements

Atomic Number
Symbol
Name
Atomic Mass

1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.008																	2 He Helium 4.003
3 Li Lithium 6.941	4 Be Beryllium 9.012											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.982	14 Si Silicon 28.086	15 P Phosphorus 30.974	16 S Sulfur 32.066	17 Cl Chlorine 35.453	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.956	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.631	33 As Arsenic 74.922	34 Se Selenium 78.972	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.95	43 Tc Technetium 98.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.906	46 Pd Palladium 106.42	47 Ag Silver 107.868	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.711	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.904	54 Xe Xenon 131.294
55 Cs Cesium 132.905	56 Ba Barium 137.328	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.948	74 W Tungsten 183.84	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.217	78 Pt Platinum 195.085	79 Au Gold 196.967	80 Hg Mercury 200.592	81 Tl Thallium 204.383	82 Pb Lead 207.2	83 Bi Bismuth 208.980	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [280]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [294]	118 Og Oganesson [294]

Lanthanide Series	57 La Lanthanum 138.905	58 Ce Cerium 140.116	59 Pr Praseodymium 140.908	60 Nd Neodymium 144.242	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 158.925	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.055	71 Lu Lutetium 174.967
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.038	91 Pa Protactinium 231.036	92 U Uranium 238.029	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium 247.070	97 Bk Berkelium 247.070	98 Cf Californium 251.080	99 Es Einsteinium [254]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.101	103 Lr Lawrencium [262]

Besides organizing elements based on atomic numbers, the periodic table provides an organized structure that helps define categories of elements. The rows of the periodic table are called **periods**, which define the highest energy level an electron of that element occupies at rest. The columns of the periodic table are called **families** that share valence electron configurations.

Physical properties of elements are shared in periods and families, with families generally having stronger effects than periods. For example, when you move right to left and top to bottom on the periodic table elements become more metallic. These physical properties are due to the electron configurations. The **atomic radius** gets larger as you move down a family or from left to right across a period. This is because there are more electron shells as you move down the period and the diameter of these shells contracts when the valence shell becomes occupied.

On the other hand, the **ionization energy** increases as you move from left to right and from bottom to top. This is due to the higher stability of electron shells closer to the nucleus and the higher magnetic pull of nuclei with more positively charged protons on negatively charged electrons. In the free response section, you may be asked to explain the basis for periodic trends.

You should be familiar with the basic families on the periodic table and their features:

Alkali metals (1): These are shiny, soft, and very reactive. All have their outer electron in an s-orbital that reacts easily. They are never found uncombined in nature, as they are highly reactive. They react violently with water, causing an explosion. These often lose one electron to take on a +1 charge.

Alkaline earth metals (2): These are shiny, silver-white metals that are semi-reactive. The outermost s orbital is full, so they can form cations with a charge of +2. These are known to react with halogens and form ionic halides, and all but Beryllium react with water to form a hydroxide and hydrogen gas. These often lose two electrons to take on a +2 charge.

Transition metals: These have a partially filled d sub-shell, so they can form cations with an incomplete valence shell. These are less reactive, so are often found uncombined in nature. These can conduct electricity, form magnets, and make compounds with color.

Chalcogens (16): These have 6 electrons in their outer shell, so often form anions with a -2 charge. These form compounds through covalent bonding.

Halogens (17): These have 7 electrons in their valence shell, so they tend to form anions in water with a -1 charge. These tend to form compounds with covalent bonds or are found as highly reactive diatomic molecules. When combined with hydrogen, these form strong acids.

Noble gasses (18): These are virtually unreactive, colorless, odorless, gases. These have a full octet of valence electrons, so are found uncompounded in nature and are difficult to get to form reactions.

Valence Electrons and Ionic Compounds

When the **valence shell** is not full, electrons in this shell can interact with other atoms by forming **ionic bonds**. An ionic bond forms when an atom donates a valence electron to another atom, typically a metal and a non-metal. The atom that loses an electron becomes a positively charged cation, and the atom that gains an electron becomes a negatively charged anion.

The opposite charges of the atoms attract them together, causing an ionic bond to form. Ionic bonds help to increase the stability of the atoms involved by having the optimal number of electrons in the valence shell. The first five elements in the periodic table are most stable when they have 2 electrons in their 1s orbital; this is called the **duet** rule. Thus, in ionic compounds, these elements aim to gain or lose enough electrons to have two total. For most elements with more than 5 protons, the optimal configuration is to have eight electrons in the valence shell; this is called the **octet rule**.

In ionic compounds these atoms will gain or lose electrons, to have a total of eight in their valence shell. As mentioned previously, columns on the periodic table are organized by the number of valence shell electrons. Thus, elements in the same column tend to have similar charges as ionic compounds and will tend to form analogous compounds (e.g., NaCl and KCl).

Outside Reading

- For more information on atomic structure and mass:
    - https://courses.lumenlearning.com/boundless-chemistry/chapter/the-structure-of-the-atom/
    - https://dlc.dcccd.edu/biology1-2/atoms-and-elements
- For more information on mass spectroscopy:
    - https://www.chemguide.co.uk/analysis/masspec/howitworks.html
- For more information on photoelectron microscopy:
    - https://www.khanacademy.org/science/chemistry/electronic-structure-of-atoms/electron-configurations-jay-sal/a/photoelectron-spectroscopy
- For more detailed information periodic trends:
    - https://courses.lumenlearning.com/boundless-chemistry/chapter/periodic-trends/
- For further reading on ionic compounds:
    - https://courses.lumenlearning.com/introchem/chapter/ionic-bonds/

Atomic Structure and Properties Questions

Water has a molecular mass of 18 and has one atom of oxygen to two atoms of hydrogen. Which of the following choices is the procedure to calculate the mass ratio of hydrogen to oxygen in water?

A. $\frac{2}{18} = 0.111$

B. $\frac{2}{16} = 0.125$

C. $\frac{16}{18} = 0.888$

D. $\frac{16}{2} = 8.000$

Explanation:

The correct answer is B. Water (molecular mass 18) has one atom of oxygen (atomic mass 16) to two atoms of hydrogen (atomic mass 1). The mass ratio of hydrogen to oxygen in water is $\frac{2}{16} = 0.125$.

A 100-g sample of $CaCO_3$ (FW = 100 g/mol) was heated at 500°C for 12 hours. Afterwards, the remaining solid was found to have a weight of only 56 g. Which balanced chemical equation best describes the reaction that took place?

A. $CaCO_{3(s)} + \text{heat} \rightarrow CaCO_{(s)} + O_{2(g)}$

B. $2CaCO_{3(s)} + \text{heat} \rightarrow 2CaC_{(s)} + 3O_{2(g)}$

C. $CaCO_{3(s)} + \text{heat} \rightarrow CaO_{(s)} + CO_{2(g)}$

D. $CaCO_{3(s)} + \text{heat} \rightarrow 2CaO_{2(s)} + CO_{(g)}$

Explanation:

The correct answer is C. The molecular weight of $CaCO_3$ is 100 g/mol, meaning one mole of material was heated. The remaining solid must also represent one mole of material and have a molecular weight of 56 g. CaCO has as molecular weight of 68 g/mol.

Which of the following electron configurations is isoelectronic to Cl^-?

A. $1s^2 2s^2 2p^6 3s^2 3p^3$

B. $1s^2 2s^2 2p^6 3s^2 3p^4$

C. $1s^2 2s^2 2p^6 3s^2 3p^5$

D. $1s^2 2s^2 2p^6 3s^2 3p^6$

Explanation:

The correct answer is C. Isoelectronic means having the same electrons. Chlorine has 17 electrons and the chloride ion has one more (18). This answer has 18 electrons.

Molecular and Ionic Compound Structure and Properties

Around 7–9% of the questions on your AP exam will cover Molecular and Ionic Compound Structure and Properties.

Types of Chemical Bonds

Chemical bonds are the attractive forces between atoms that hold them together, including sharing electrons and other electrostatic forces. These forces can be **intramolecular**, as in they occur *within* a molecule, or **intermolecular**, as in occurring *between* molecules. Intramolecular forces are stronger than intermolecular forces. The main types of intramolecular binding forces are summarized in the following table.

Bond	Description	Example
Covalent	The sharing of electrons between a pair of atoms, also called a molecular bond. Covalent bonds can result in atoms having complete valence shells, stabilizing the atoms. These are usually gasses, liquids, or soft solids and include most biological molecules. The first covalent bond is called a sigma bond (σ) and additional bonds are called pi bonds (π). The sigma bond is the most stable.	CO_2
Ionic	Ionic bonds describe the electrostatic attraction between cations and anions or with charged polyatomic ions. Ionic bonds involve the transfer of electrons from a metal to a non-metal, resulting in full valence shells for both atoms. Ionic bonds tend to be easily separated by external forces, like the addition of polar solvents, causing substances to break apart into anions and cations. Solid, ionically bonded structures form ordered and strong lattices that are non-conductive and have high melting and boiling points. This group includes salts.	NaCl
Metallic	Metallic bonds are the sharing of free electrons in a metallic structure, composed of charged cations. In metallic bonds, valence electrons are only loosely bound to the nucleus and form a sort of cloud around metallic cations, allowing them to be shared. This results in a highly stable configuration of positively charged cations in a sea of negatively charged electrons. Metallic bonds account for certain features of metals like malleability, conductivity, and strength.	Copper wire, aluminum foil

One way to predict whether a bond is ionic or covalent is to look at the **electronegativity** of the atoms involved. Electronegativity describes how much an atom attracts bonding electrons. The scale runs from 4 (fluorine) at the high end to 0.7 (cesium and francium) at the low end. On the periodic table, electronegativity increases from left to right and bottom to top (excluding noble gasses).

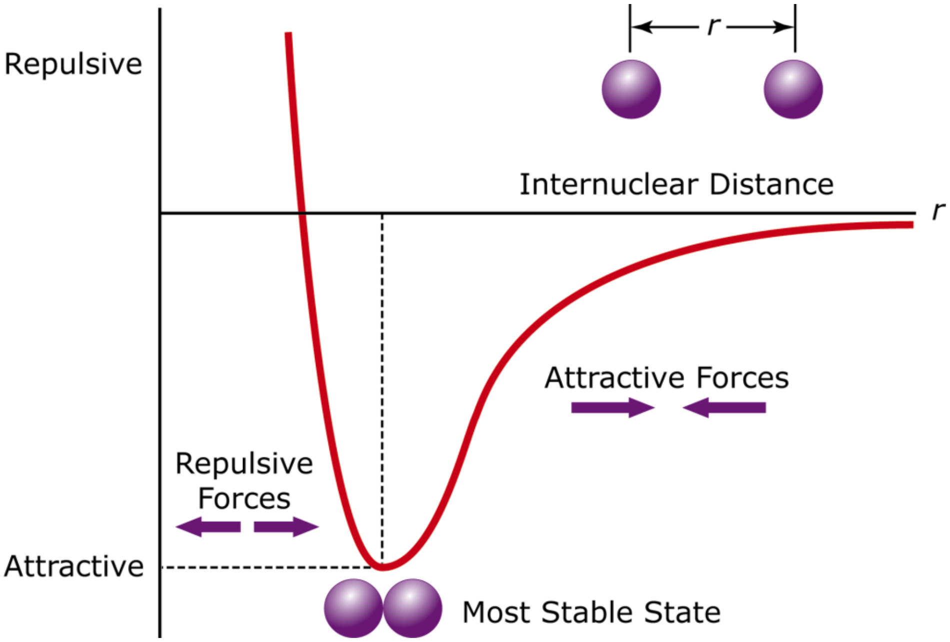
Another way to think of electronegativity is as a quantitative way to consider how factors like the atomic structure, valence shells, and Coulomb's law affect attraction between ions. To determine bond type, remember that when the difference between electronegativity is high (greater than 1.7), ionic bonds form. When the difference is low (1.7 and lower), covalent bonds form.

Covalent bonds formed between atoms with similar electronegativities (<0.5) are **non-polar covalent bonds**. This means that electrons are shared equally across the atoms. A **polar covalent bond** forms when there is a larger difference in electronegativity across atoms. The atom with the greater charge pulls electrons closer to it, forming a **dipole**. In a dipole, electrons spend more time at one end of the molecule, giving that side a slightly more negative charge (δ-) and the other end a slightly positive charge (δ+). This can result in molecules that are charged, or polar, and can interact with other molecules through these charges.

The size of a dipole is measured by the **dipole moment**, μ. When the difference between the dipole is very high, the molecule at the δ+ end of the bond essentially transfers its electrons to the more electronegative atom, forming an ionic bond. The direction of a dipole is indicated in a bond as an arrow from the less electronegative atom to the more electronegative atom.

Intramolecular Force and Potential Energy

During covalent bond formation, unstable atoms with incomplete valence shells share electrons to increase their stability. Attractive forces between the nuclei and electron clouds of unstable atoms attract each other to form a bond. This is counteracted by repulsive forces between each atom's nuclei and between each atom's electron clouds. This balance between repulsive and attractive intramolecular forces can be shown in a potential energy diagram.



In this diagram, when the two molecules are far apart there is no **potential energy**, or stored energy. The closer the molecules get to each other, the lower the potential energy due to attractive forces between the molecules (remember Coulomb's law). The distance where this potential energy is lowest is the average length of the covalent bond that forms between them. In other words, covalent bond lengths are optimal when the potential energy of the bond is lowest. You'll notice in the diagram that when the molecules get even closer together, the potential energy rapidly shoots back up. This is due to repulsive intramolecular forces between the atoms. In the case of double and triple bonds, the bond length becomes shorter and the strength of the bond becomes higher; thus, you can expect to see shorter lengths between nuclei and higher bond energies.

Structure of Ionic Solids

Ionic solids form in a manner that reduces the repulsive forces between similarly charged ions and increases the attractive force between oppositely charged ions. This forms a chemical lattice with an orderly arrangement. The **lattice energy (*E*)** is the energy needed to separate 1 mol of an ionic solid into its gas phase. This is proportional to the product of the electrical charges of the ions (*Q*) divided by the sum of the radii of the atoms (*r*):

$$E \propto \frac{Q_1 Q_2}{r}$$

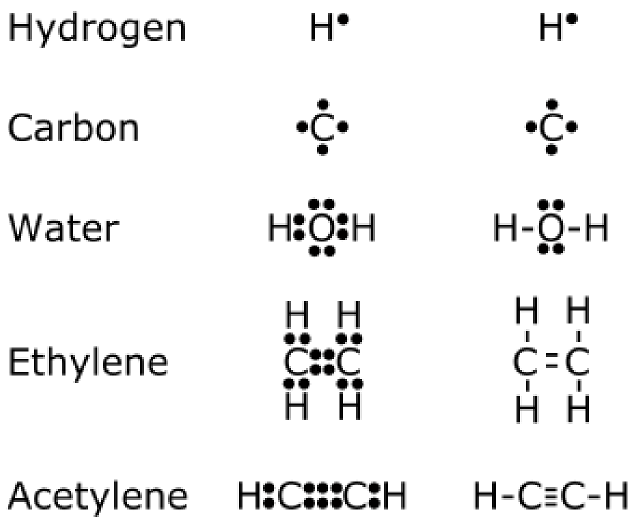
Note that when the ions are oppositely charged, the lattice energy is negative. This indicates energy will be released when the lattice forms due to attraction between the molecules. The more negative the lattice energy is, the stronger the ionic bonds will be. These strong bonds holding ionic solids together explains some of the features of ionic solids such as crystal structures and brittle properties.

Structure of Metals and Alloys

Metallic solids are formed by an array of metallic cations surrounded by a sea of freely moving shared electrons. The loose shared electron sea helps to understand some of the features of pure metals, such as conductance, malleability, and ductility. When metals are mixed with other metals or non-metals, **alloys** are formed. When two metals of similar size are mixed, a **substitutional alloy** is formed. The percentages of metals in a substitutional alloy can be varied to alter the properties of the alloy, such as increasing strength and conductivity while decreasing corrosion. When a pure metal is mixed with a much smaller metal or non-metal, an **interstitial alloy** is formed. Interstitial alloys are stronger, harder, and less ductile than their pure host metals.

Lewis Diagrams

Lewis dot diagrams are a quick way to represent the valence electrons of an atom, where each dot around a molecule represents a valence electron. A covalent bond is represented by dots between atoms, or by dashes corresponding to the number of covalent bonds. According to the octet rule, most atoms are considered stable when this valence shell is occupied by eight atoms; thus, the optimal configuration is to have 2 electrons on each of the 4 sides or 4 total bonds. Hydrogen atoms only need two electrons in their valence shells.



When drawing a dot diagram for a compound, first arrange the ions so they form a symmetrical structure. Remember that hydrogen is always on the outside of the structure, never central. Then calculate the total number of valence electrons the molecule has vs. the number of molecules needed (generally 8 for every molecule except hydrogen). The difference between the number of electrons the molecule has and the number needed tells you how many electrons are shared. Then divide shared electrons by two to find out how many are between elements in this molecule. You then draw the bonds and complete the structure by adding the remaining electrons so that each atom has the correct number of valence electrons.

Lewis dot diagrams do not handle unpaired electrons well or show the difference between the strength of bonds; these cases are better described by models that take into account 3-D structure.

Resonance and Formal Charge

Resonance structures are not adequately represented by dot diagrams. These are instance where two forms of a molecule are possible with the same connectivity but with differences in the distribution of electrons. For instance, ozone can exist as O=O–O or O–O=O. In reality, these would exist as partial bonds, but for the purpose of demonstration would be written as follows:

O=O–O ⇔ O–O=O.

You may come across instances where there are multiple possible Lewis structures. To determine which is the most appropriate, you can calculate the **formal charge** of the atoms in the chemical compound:

$$\text{Formal charge} = (\#\ \text{valence electrons}) - \left(\#\ \text{nonbinding electrons} + \frac{\text{bonding electrons}}{2}\right)$$

The most favorable Lewis structures will have small formal charges on each element: more electronegative elements will have lower formal charges, like charges will be far apart, and unlike charges will be near. The total formal charge for the molecule is the sum of the formal charges of the atoms.

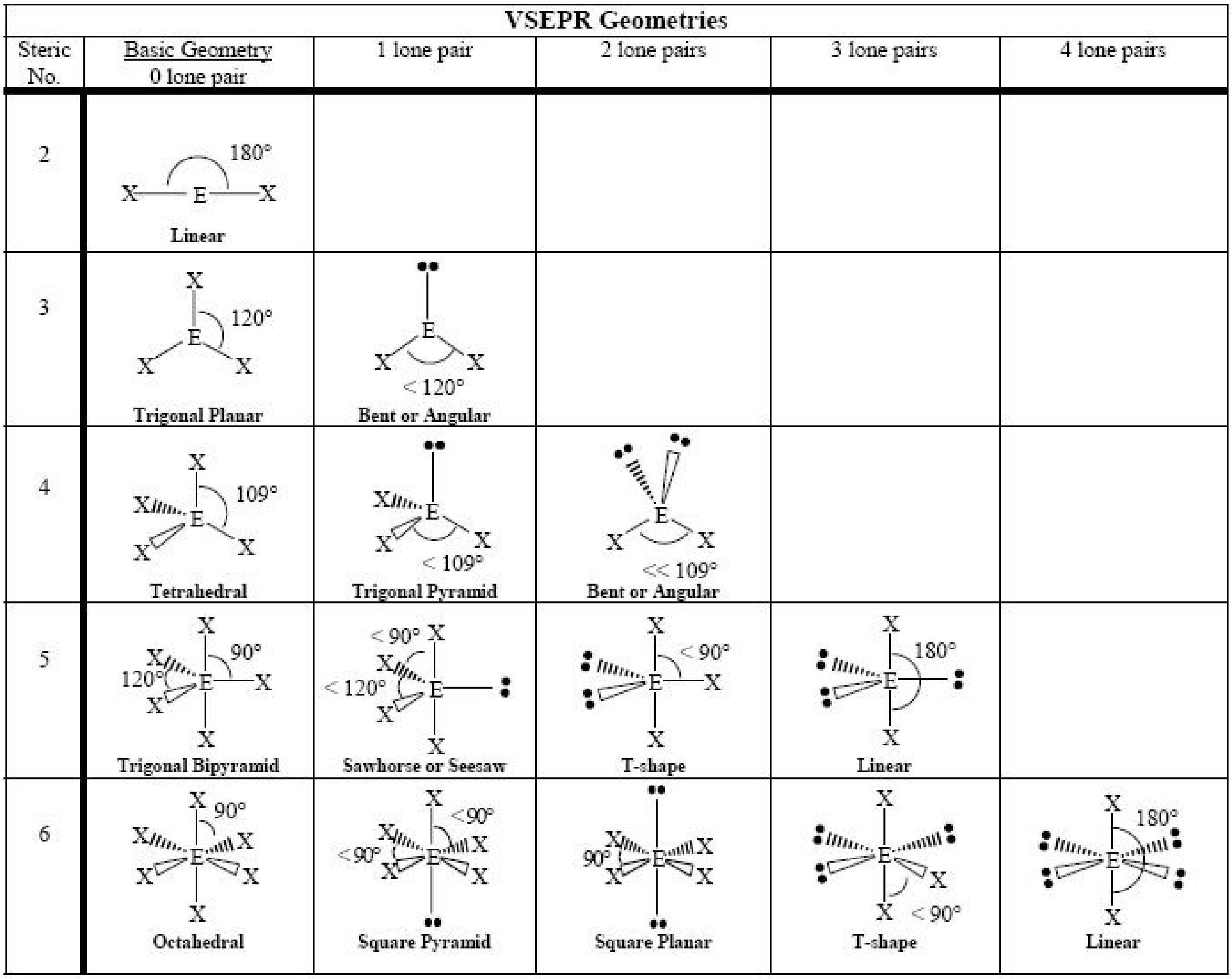
Note that you may be asked on the exam to compare the relative contribution of different resonance structures possible for a molecule. In that case, the resonant structures that are more common are those that satisfy the octet (or duet) rule for all atoms that have a formal charge on each atom closest to zero, and where more electronegative elements have lower formal charges.

VSEPR and Bond Hybridization

Valence shell repulsion theory, or VSEPR, asserts that electron pairs repel each other and unbonded electrons are even more repulsive to bonded pairs. This causes molecules to take on distinct shapes depending on the number of bonds and hybridized orbitals. For example, a molecule with two sigma bonds will take on a linear shape so that both bonds will be as far apart as possible. A molecule with four bonds will take on a tetrahedral shape to optimize distance.

You will need to estimate molecular shape for the exam using VSEPR. To determine the shape of a chemical compound using VSEPR:

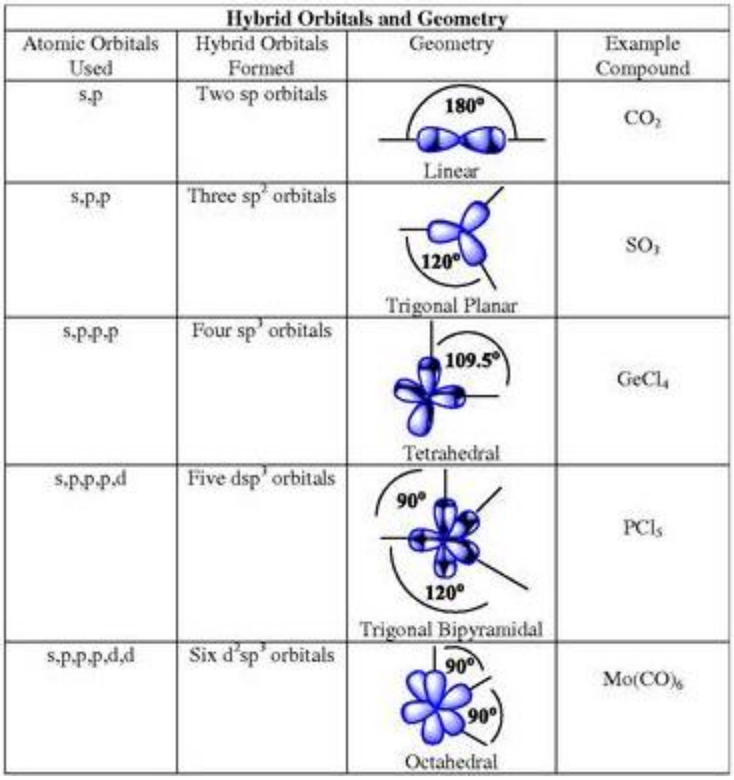
1. Draw out the Lewis dot diagram.
2. Count the number of electron-dense regions. These include each element in the compound as well as each pair of electrons.
3. Mentally arrange these electron dense regions to allow equal space between them; this gives the overall shape of the structure
4. Take into account **electronic geometry**, due to the number of lone electron pairs, as well as **molecular geometry**, due to the number of bonds.



VSEPR Geometries

Steric No.	Basic Geometry 0 lone pair	1 lone pair	2 lone pairs	3 lone pairs	4 lone pairs
2	180° Linear				
3	120° Trigonal Planar	< 120° Bent or Angular			
4	109° Tetrahedral	< 109° Trigonal Pyramid	<< 109° Bent or Angular		
5	90° 120° Trigonal Bipyramid	< 90° < 120° Sawhorse or Seesaw	< 90° T-shape	180° Linear	
6	90° Octahedral	< 90° < 90° Square Pyramid	90° Square Planar	< 90° T-shape	180° Linear

Another way to represent molecular geometry is through **Valence bond theory.** In this theory, covalent bonds form through the mixing of orbitals to form **hybrid orbitals**. The number of hybrid orbitals formed is equal to the number of contributing orbitals. The types of orbitals that contribute determine the hybrid orbital type (e.g., s and p orbitals hybridizing means that you will have two sp orbitals).



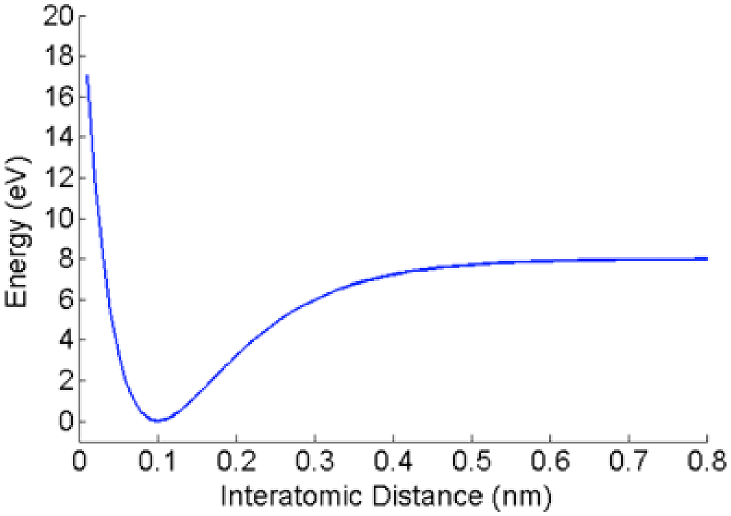
Hybrid Orbitals and Geometry

Atomic Orbitals Used	Hybrid Orbitals Formed	Geometry	Example Compound
s,p	Two sp orbitals	180° Linear	CO_2
s,p,p	Three sp^2 orbitals	120° Trigonal Planar	SO_3
s,p,p,p	Four sp^3 orbitals	109.5° Tetrahedral	$GeCl_4$
s,p,p,p,d	Five dsp^3 orbitals	90° 120° Trigonal Bipyramidal	PCl_5
s,p,p,p,d,d	Six d^2sp^3 orbitals	90° 90° Octahedral	$Mo(CO)_6$

Outside Reading

- For more information on bonds, see:
    - https://www.chemguide.co.uk/atoms/bondingmenu.html#top
    - https://www.visionlearning.com/en/library/Chemistry/1/Chemical-Bonding/55
- For more details on VSEPR theory:
    - https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/09._Molecular_Geometry_and_Bonding_Theories/9.2%3A_The_VSEPR_Model
- For an in-depth explanation of hybrid orbitals, see:
    - https://chem.libretexts.org/LibreTexts/University_of_Kentucky/UK%3A_General_Chemistry/08%3A_Advanced_Theories_of_Covalent_Bonding/8.2%3A_Hybrid_Atomic_Orbitals

Sample Molecular and Ionic Compound Structure and Properties Questions



When two chlorine atoms are brought together, they form a Cl–Cl bond and energy is released. The potential energy for this system as a function of Cl–Cl distance is shown above. According to this graph, what amount of energy is required to break the Cl–Cl bond?

A. 17 eV
B. 8 eV
C. 0 eV
D. −8 eV

Explanation:

The correct answer is B. The right side of the graph asymptotically approaches 8 eV, which is the energy required to separate the two Cl atoms infinitely far apart.

Which of the following hydrocarbons is expected to have single bonds between all carbon atoms?

A. propane (C_3H_8)

B. butene (C_4H_8)

C. hexene (C_6H_{10})

D. octyne (C_8H_{14})

Explanation:

The correct answer is A. All of the bonds between the carbon atoms are the same (single bonds). The ending –ene signifies there are double bonds between carbon atoms along with single bonds and the ending –yne signifies there are triple bonds, which can be seen by drawing the Lewis diagram.

Which of the following statements best explains why LiBr is expected to boil at a higher temperature than SF_4?

A. LiBr contains ionic bonds and SF_4 has dipole-dipole forces

B. The density of SF_4 is greater than that of LiBr

C. SF_4 has a higher molar mass than LiBr

D. LiBr is linear and SF_4 is not

Explanation:

The correct answer is A. LiBr forms an ionic bond, because Li is a very active metal and Br is a very electronegative nonmetal. SF_4 is a polar molecule with dipole-dipole forces between the molecules. Generally, species with ionic bonds have higher boiling points than species with dipole-dipole forces.

Intermolecular Forces and Properties

Around 18–22% of the questions on your AP exam will cover Intermolecular Forces and Properties.

Intermolecular Forces

Intermolecular forces describe the attractive and repulsive forces between molecules. Intermolecular forces are not chemical bonds; rather, they are the forces between bonded molecules and other molecules or ions. These include a variety of forces including hydrogen bonds, dispersion forces, and dipole interactions.

London dispersion forces are temporary and weak forces that occur due to Coulombic interactions. These occur when electrons from two atoms are positioned to create temporary dipoles. Dispersion forces are larger for molecules with more electrons and increase when there is more contact area between molecules. All molecules have dispersion forces. Although they are individually small, they can add up across a molecule to be large. One temporary dipole can induce other dipoles to occur nearby. The collective induction causes polar substances to freeze when temperatures are lowered, as in the case of water turning into ice.

Dipole-Dipole interactions are interactions between two polar molecules. Here, the partial positive side of one molecule is attracted to the partial negative side of another molecule. Dipoles can also induce temporary dipoles in non-polar molecules. These **dipole-induced dipole** interactions can increase the solubility of non-polar molecules in water.

Hydrogen bonds are attractive forces between an electronegative atom and hydrogen atom that is bound to an electronegative atom (N, O, or F). The most common example of a hydrogen bond is between two water molecules. This is an example of a dipole-dipole interaction, where the hydrogen end of one water molecule (δ+) interacts with the oxygen from another molecule (δ-).

Solids, Liquids, and Gases

Matter exists in three primary states, or phases, on Earth: solid, liquid, or gas. States of matter can change due to temperature or pressure. Solids and liquids are relatively incompressible. Solids have a definite shape while liquids will take the form of whatever container they are put in over time. Gasses, on the other hand, are compressible and will fill any shape that they are held in. While molecules in solids and liquids have constant contact with neighboring molecules, gas molecules do not. This means that properties of solids and liquids are dependent on intermolecular forces, while gasses are not.

There are two forms of microscopic solids: amorphous solids and crystalline solids. **Amorphous solids** are solids that lack a definite organization. These solids do not have a definite melting point; rather, they decrease in viscosity when the temperature increases. Amorphous solids include substances like glass and rubber.

Crystalline solids have crystal lattice structures with an organized microscopic appearance. These include ionic, metallic, molecular, and atomic solids as well as covalent network solids. Covalent network solids are crystal lattices where molecules are joined by covalent bonds, thus forming one giant molecule. Diamonds and graphite are examples of crystal lattices. You should be familiar with the properties of different types of solids and how they relate to intermolecular properties for the AP exam.

Molecules in liquids form very brief interactions with their neighbors, thus intermolecular forces are momentary; however, liquids do have three unique and notable macroscopic properties. Molecules within a liquid are very attracted to each other due to **cohesive forces**. This means that molecules at the surface of a liquid are constantly drawn towards the liquid molecules below. The result of this is a flattening at the air-liquid interface, noticeable in a pool of liquid as well as in droplet formation. The cohesive forces also cause liquids to resist increasing surface area at the air-liquid interface—this is called **surface tension**.

Viscosity is the resistance of liquids to flow. This is caused by the strength of intermolecular forces between liquid molecules. The stronger the intermolecular forces, the more viscous the liquid. Finally, when liquids are placed in narrow chambers, like tubes, another property, called **capillary action**, becomes apparent. Capillary action is a rising of a liquid in a tube against the force of gravity. This occurs due to the attractive forces between the liquid and the solid walls of the tube, called **adhesive forces**. The stronger the attraction between liquid and solid, the higher the rise will be.

Ideal Gas Law

Gases have no fixed volume or shape. The molecules within gasses are able to freely expand, to fill any space. Due to the large spacing of molecules in gasses, they tend to behave in similar ways regardless of type of gas. Thus, a set of equations can be used to describe the relationships between pressure (*P*), volume (*V*), temperature (*T*), and number of molecules (*n*) of a gas. Equations that describe how these properties relate, called **ideal gas laws**, are described in the following table.

Law	Description	Equations
Boyle's Law	Pressure is inversely related to volume when temperature and number of molecules are constant. For example, imagine a fixed amount of gas trapped in a sealed container at a constant temperature. If you then increase the volume (V_1) of the container to V_2, the molecules will have more room to move around within the container, increasing the pressure (P_1) to P_2.	$V \propto \frac{1}{P}$ & $P \propto \frac{1}{V}$ or $P_1V_1 = P_2V_2$
Charles' Law	Volume is proportional to temperature when pressure and number of molecules of gas are held constant. If pressure and number of molecules are held constant, a rise in temperature (T_1) to T_2 will cause a proportional rise in volume of the container (V_1) to V_2.	$V \propto T$ or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$
Guy-Lussac's Law	Pressure is proportional to temperature when volume and number of molecules of gas are held constant. If you now hold the volume and n constant, and increase the temperature (T_1 to T_2), the pressure will rise proportionally from P_1 to P_2.	$P \propto T$ or $\frac{P_1}{T_1} = \frac{P_2}{T_2}$
Avogadro's Law	Volume is proportional to the number of gas molecules, when temperature and pressure are constant. If the container is filled with more molecules (n_1 to n_2), while the temperature and pressure are held constant, the volume of the container will increase (V_1 to V_2) to accommodate the additional particles.	$V \propto n$ or $\frac{V_1}{n_1} = \frac{V_2}{n_2}$
Ideal Gas Law	A combination of the three gas laws that describes how the properties of a perfect theoretical gas relate to each other. R is the empirically determined gas constant (R = 8.3145 $\frac{kPa\cdot L}{\text{mol}\cdot K}$). For an ideal gas, $\frac{PV}{nRT} = 1$	$PV = nRT$ or $\frac{P_1V_1}{n_1T_1} = \frac{P_2V_2}{n_2T_2}$
Dalton's Law of Partial Pressures	The total pressure of gasses in a mixture is equal to the sum of the pressures of the individual gasses. The partial pressure of a gas is equal to the total pressure of the mixture multiplied by the mole fraction (X) of the gas.	$P_{\text{total}} = P_A + P_B + P_C \dots$ $P_A = P_{\text{total}} \times X_A$ where $X_A = \frac{\text{moles } A}{\text{total moles}}$

As the number of molecules in a substance (*n*) can be quite large, it is easier to define them based on moles. As discussed above, moles are related to mass using the equation:

$$\#\text{ of moles} = \frac{\text{Weight in Grams}}{\text{Atomic Mass}}$$

For gasses, the number of moles is calculated based on volume rather than weight, based on a similar equation:

$$\#\text{ of moles} = \frac{\text{Volume}}{\text{Molar Volume}}$$

In other words, the molar volume is equal to the volume that one mole occupies in set temperature and pressure conditions. For ideal gasses the **standard molar volume** is 22.4 L. This is the volume one mole of an ideal gas occupies at 273.15 K and 1 atm of pressure. Given the equation and the ideal gas laws, the molar volume can be calculated for any temperature and pressure:

$$\text{Molar volume} = \frac{V}{1\text{ mole}} = \frac{RT}{P}$$

Ideal gas equations ignore effects between molecules that real gasses have but are a good approximation of relationships between properties at high temperatures and low pressures. In conditions where intermolecular forces are higher, such as low temperatures and high pressures or when describing molecules with high intermolecular forces, the ideal gas laws lead to errors.

Kinetic Molecular Theory

Kinetic molecular theory (KMT) describes how gas particles behave in order to explain the overall properties of gasses. In KMT, gasses are made primarily of empty spaces that contain molecules that are constantly moving independently of the neighboring molecules. Here are the important points of KMT:

- Gas is made of tiny molecules whose total volume is much smaller than the volume of the gas. Put another way, the distance between molecules in a gas is much greater than the size of individual molecules.
- The molecules in a gas have no attractive forces between them, or with the container that holds them.
- Individual molecules are constantly moving in a random direction until they collide with another molecule or with the container. These collisions are completely elastic, as in no change in energy occurs due to a collision. In other words, if one molecule slows down due to a collision, the other molecule will speed up an equal amount so there is no net loss of energy.

- The average **kinetic energy** of the gas is solely determined based on the absolute temperature. All gasses have the same average kinetic energy at a given temperature.

Kinetic energy (E_k) is dependent on mass (m) and velocity (v) of a molecule:

$$E_k = \frac{1}{2}mv^2$$

Molecules of a gas have an average kinetic energy, but individual molecules can have different velocities. When the number of molecules at each velocity are plotted, they fit along a **Boltzmann distribution**. This distribution represents several important properties of gasses. For example, the peak of the distribution corresponds to the most probable velocity of a molecule. The distribution of velocities changes according to temperature for a given molecule, where higher temperatures have broader distributions of velocities with higher average velocities.

Solutions and Mixtures

Solutions are homogenous mixtures of substances that are not physically bonded. In solutions, **solutes** are dissolved into **solvents**. Solutions can involve different states of matter dissolving into another. For instance, sugar can be dissolved into water, carbon dioxide can dissolve into a drink to make soda, and metal alloys are solid metal solutions.

Concentration is expressed in several ways. Some common expressions are:

$$\text{Molarity (M)} = \frac{\text{Moles}}{\text{Liter}}$$

$$\text{Molality} = \frac{\text{Moles}}{\text{Kilogram}}$$

$$\text{Mole Fraction} = \frac{\text{Moles}}{\text{Total Moles of Solution}}$$

$$pH = -\log[H^+]$$

For the AP exam, be sure that you can use these equations to calculate the number of particles in a solution, molarity, and volume. Also, be prepared to represent these graphically by showing the relative abundance of particles in a solution and how different particles may interact.

Separation of Solutions and Mixtures Chromatography

Components of solutions can be physically separated using evaporation, distillation, or chromatography.

In **evaporation**, aqueous or volatile solvents are evaporated or gently boiled away to recover the solute—this works in the case of recovering sodium chloride from salt water.

In **distillation**, different vapor pressures and boiling points are used to separate solutes from a solution. In this method, the solution is placed in a round bottom flask equipped with a condenser and a receiving vessel. The flask is heated to the boiling point of the more volatile component in the mixture. It then vaporizes and is collected in the condenser, where it returns to liquid phase and is collected in the receiving vessel.

In **chromatography**, liquid mixtures are separated by taking advantage of the differences between the intermolecular forces of components in liquid (mobile phase) with absorbent paper or silica gel (stationary phase). The molecules in the solution will interact differently with the solvent than they will with a solid, polar substance; thus, when the stationary phase is placed into the mobile phase, the components will travel at different speeds along the stationary phase.

Solubility

Factors that affect **miscibility**, the ability of a solute to be soluble in a solution, are solute-solvent interactions, concentration, temperature, and pressure. The attraction between a solute and a solvent can determine the solubility. In general, like molecules attract like so polar substances dissolve in other polar solutes and non-polar substances dissolve in non-polar solutes. The effect of concentration is described by the **common-ion effect**, wherein adding more of an ion to a solute where that ion already exists decreases the solubility of additional ions. When the solution is **saturated**, the solid solute is at equilibrium with the dissolved solute, and additional solute cannot be dissolved.

Temperature affects solutes differently depending on whether the solvation reactions are **endothermic** ($\Delta H_{\text{solvation}} > 0$) or **exothermic** ($\Delta H_{\text{solvation}} < 0$). In endothermic reactions, the solubility of solids into liquids increases when temperature increases. In exothermic reactions, the solubility of solids into liquids decreases when temperature increases. For gases dissolved in liquids, increases in temperature decrease solubility; this is why sodas tend to get flat when heated.

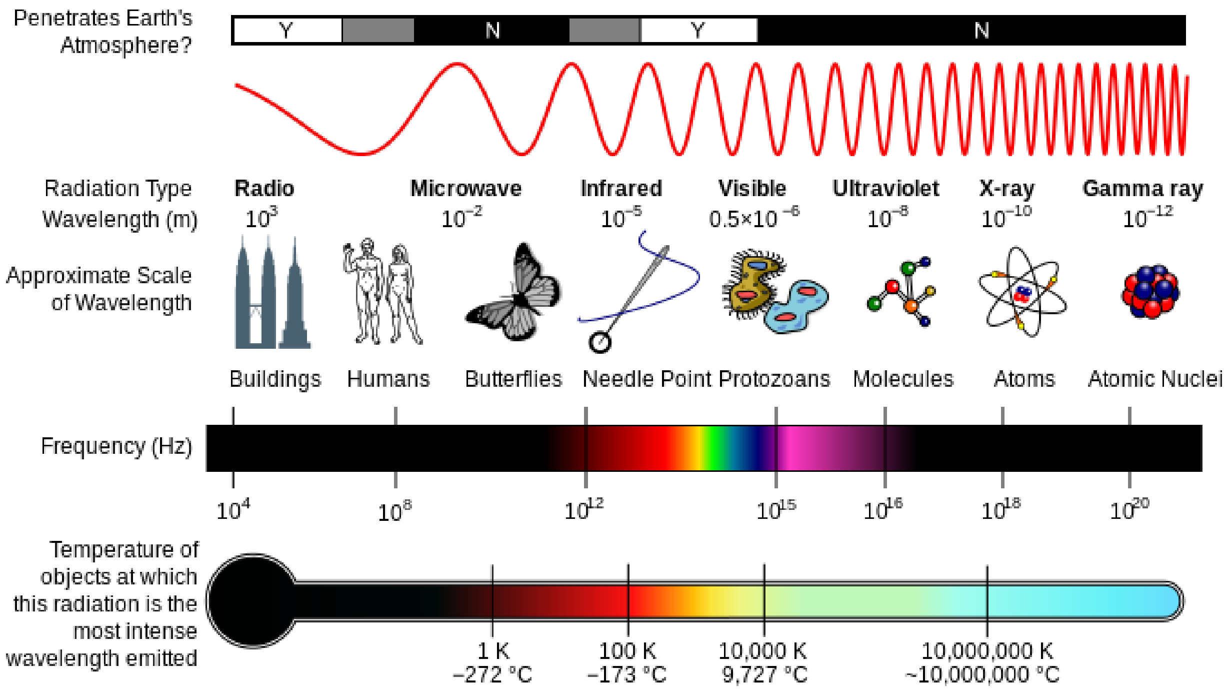
Pressure can affect the solubility of gasses in liquids according to **Henry's law,** which states that when temperature is constant, the amount of gas that can dissolve in a liquid (C) is proportional to the partial pressure of the gas (p):

$$p = k_h C$$

In this equation, C is the molar concentration of gas in the solution expressed in mol/L, and k_h is Henry's law constant, expressed in L atm/mol, which depends on the gas molecule.

Spectroscopy and Electromagnetic Spectrum

Atoms or molecules can absorb or emit energy and depending on the amount of energy absorbed or emitted, different effects can occur. These effects depend on what frequency on the electromagnetic spectrum the energy absorbed or emitted lies. The **electromagnetic spectrum** describes the range of energy frequencies that exist and how they relate to wavelength and energy level.



For example, when an atom is energized by the absorption of UV light, electrons in the atom’s shell undergo an energy level transition to a higher orbital. When the electrons return to a resting state, they will emit photons of light that correspond to the change in energy level. This is the basis of spectroscopy, which can be used to analyze the unknown chemicals in a sample. When atoms absorb energy at levels lower than the visible spectrum, in the infrared range, the energy absorbed is not enough to induce a change in electron energy levels; rather, it can cause the chemical bonds in a molecule to vibrate at specific frequencies. This is used in infrared spectroscopy to analyze the bonds in molecules.

Photoelectric Effect

When light shines on a metal, electrons are sometimes emitted; this is called the **photoelectric effect.** This occurs because the light energy absorbed by atoms causes atoms to shift energy states. If the energy is high enough, this can cause the electron to break away and escape the atom. Different types of metals require different frequencies of light to eject electrons, depending on that metal's unique **threshold frequency.** Furthermore, the higher the frequency of light the higher the kinetic energy of emitted electrons.

Beer-Lambert Law

Beer-Lambert law describes the relationship between the amount of light absorbed by a material that the light travels through. Absorbance (A) is equal to the product of the concentration of solution (c), length of the light path (b), and the **molar absorptivity** (ε):

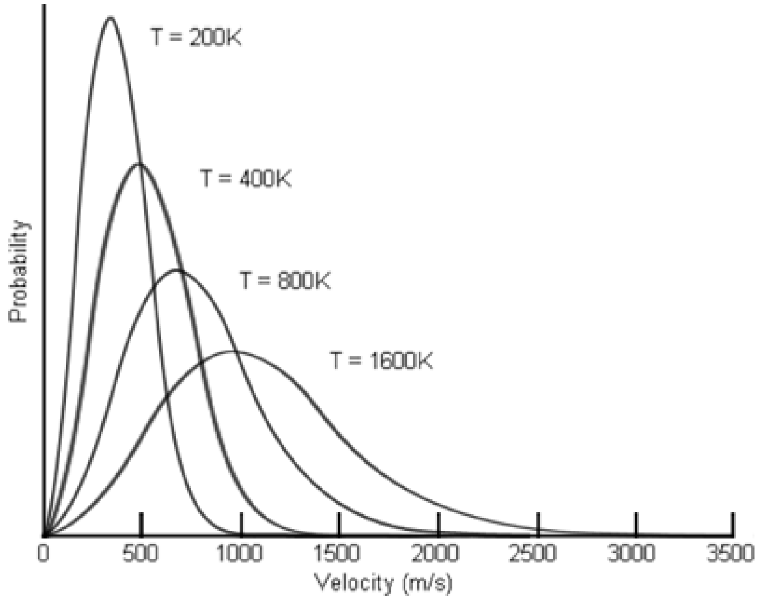
$$A = \varepsilon bc$$

Molar absorptivity describes how well a given molecule or ion absorbs light of a specific wavelength. The higher the absorptivity, the more light is absorbed in solution. Similarly, the higher the concentration of the solution (c) or the longer the path that light travels through the solution (b), the more light will interact with molecules of solute, creating more chances for light to be absorbed. In UV-spectroscopy, this equation can be used to measure the concentration of solutes in a solution.

Outside Reading

- For an explanation of kinetic energy in gasses:
    - https://opentextbc.ca/introductorychemistry/chapter/kinetic-molecular-theory-of-gases-2/
- For an explanation of how KMT relates to gas laws, see:
    - https://chem.libretexts.org/Textbook_Maps/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Physical_Properties_of_Matter/States_of_Matter/Properties_of_Gases/Kinetic_Theory_of_Gases/Basics_of_Kinetic_Molecular_Theory
- For information on how KMT relates to liquids and solids:
    - https://study.com/academy/lesson/the-kinetic-molecular-theory-properties-of-solids-and-liquids.html
- For more on Beer-Lambert law:
    - https://chem.libretexts.org/Ancillary_Materials/Reference/Organic_Chemistry_Glossary/Beer-Lambert_Law

Sample Intermolecular Forces and Properties Questions



The figure above shows the Boltzmann probability distributions of the velocities of molecules in a container at four different temperatures. Based on the figure and what you know about molecular interactions, what conclusions can you draw about the effect of temperature on reaction rate?

A. Lower temperatures increase the rate of reaction because a greater percentage of molecules travel at lower velocity, which improves the likelihood of productive collisions.

B. Lower temperatures increase the rate of reaction because more molecules will be above the minimum energy needed to react.

C. Higher temperatures increase the reaction rate because the average kinetic energy of the molecules decreases.

D. Higher temperatures increase the rate of reaction because a larger population of molecules possesses the minimum energy required for the reaction to proceed.

Explanation:

The correct answer is D. Increased temperature leads to a higher average velocity at which molecules travel. Molecules traveling at higher velocity possess greater kinetic energy which improves the likelihood that a collision will lead to a reaction.

Arrange the following molecules in order of increasing boiling point:

propane ($CH_3CH_2CH_3$), ethanol (CH_3CH_2OH), and diethyl ether (CH_3OCH_3)

A. diethyl ether < ethanol < propane

B. propane < diethyl ether < ethanol

C. diethyl ether < propane < ethanol

D. propane < ethanol < diethyl ether

Explanation:

The correct answer is B. Ethanol (b.p. 78 °C) interacts through hydrogen bonding, which is a strong type of dipole–dipole attraction. Diethyl ether (b.p. 35 °C) cannot hydrogen bond, but does associate through dipole–dipole forces. Propane (b.p. −42 °C) can only associate through weak London dispersion forces.

Which of the following pairs are most likely to be miscible, or soluble in each other?

A. CH_3CH_2OH and $CH_3CH_2CH_3$

B. H_2O_2 and CH_4

C. NH_3 and C_2H_6

D. CH_3OCH_3 and CH_3CHO

Explanation:

The correct answer is D. A solution is a homogeneous mixture. The choices include polar and nonpolar molecules. To form a solution, both molecules have to be either polar or nonpolar. Both substances are polar.

Chemical Reactions

Around 7–9% of questions on your exam will cover Chemical Reactions.

Physical and Chemical Changes

Thus far, we have discussed physical changes in chemicals—that is, changes in the state of chemicals or the creation or separation of solutions. Chemical reactions, on the other hand, transform substances into new substances, usually with different chemical compositions. Typical signs that a chemical reaction has occurred include changes like the production of heat, light, or precipitate, or changes in the color of a substance.

Net Ionic Equations

Chemical reactions are often written as linear equations with reactants on the left, products on the right, and a single or double arrow between, signifying the direction of the reaction. When balancing equations, remember:

- The **Law of Conservation of Mass** must be followed; thus, the number and types of atoms present in the reactants must also be present in the products. Make sure the number of each element in the products and the reactions are equal.
- The physical state of molecules in the reaction are denoted by subscripts as gas (g), aqueous (aq), and solid (s).
- **Molecular equations** show chemical formulas for reactants and products, but do not take into account ionization in aqueous solutions.
- **Complete ionic equations** denote molecules as ions in aqueous solution when appropriate.
- **Net ionic equations** remove spectator ions from the equation and only show molecules that participate in the reaction.

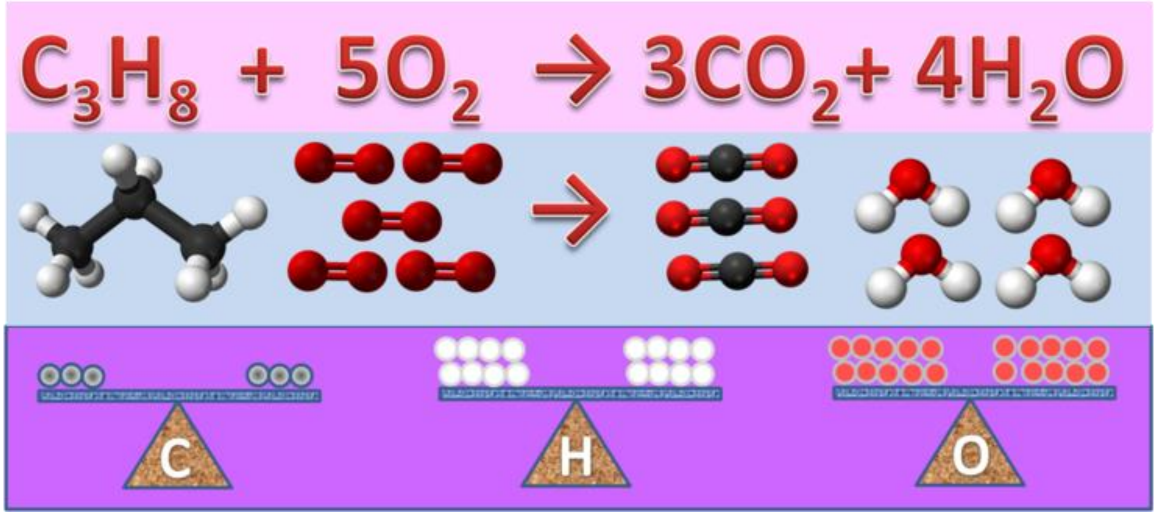
For example, consider the ionization of calcium chloride salt ($CaCl_{2\,(s)}$) in water:

$$\mathrm{CaCl_{2\,(s)}} + \mathrm{H_2O_{(aq)}} \rightarrow \mathrm{Ca^{2+}_{(aq)}} + 2\mathrm{Cl^{-}_{(aq)}} + \mathrm{H_2O_{(aq)}}$$

In this reaction, $CaCl_{2\,(s)}$ is ionized from solid to individual aqueous ions in water. The reactants consist of 1 part calcium ion, 2 parts chloride ions, and 1 part water.

To balance this equation, the reactants also must include these proportions. In this reaction, water participates as a spectator; thus, the net ionic equation would be:

$$\mathrm{CaCl_{2\,(s)}} \rightarrow \mathrm{Ca^{2+}_{(aq)}} + 2\mathrm{Cl^{-}_{(aq)}}$$



Another way to represent reactions is through the particle model. In this model showing propane combustion, each atom in the reaction is represented as a particle. To balance the reaction, make sure that all particles that are present on the reactant side are also present on the product side.

Stoichiometry

Stoichiometry deals with the quantitative relationship between elements in a reaction. Simply stated, it uses ratios of ions to calculate the amounts of reactants and products in an equation. The **factor label-method** is often used to convert ratios to molar quantities. This method uses conversion factors to convert one quantity to another quantity. This concept can be used to balance a chemical reaction, determine how many moles are present in a reaction, and even determine conversions for units of measure.

For example, we know that 1 foot = 12 inches but we would like to solve how many inches are in 0.6 feet. We can use multiplication and division to solve for this. By remembering that the units must cancel out to give the final unit, inches, we can solve this problem:

$$\frac{12\ \text{inches}}{1\ \text{foot}} \times 0.6\ \text{feet} = 7.2\ \text{inches}$$

This same concept can be used to for molar conversions. By Avogadro's number, we know that there are 6.02 × 10^{23} atoms in every mole; thus, if we want to identify the number of atoms in 0.4 moles of a substance:

$$\frac{6.02\ \times 10^{23}\ \text{atoms}}{1\ \text{mole}} \times\ 0.4\ \text{moles} = 2.41\ \times 10^{23}\ \text{atoms}$$

Similarly, we can use this concept to covert moles of substance to mass of substance and vice versa. For example, if we would like to find the mass of 5 moles of potassium, we can turn to the periodic table to find that the atomic weight of potassium is 39.098 g/mol. Thus:

$$\frac{39.098\ \text{grams}}{1\ \text{mole}} \times\ 5\ \text{moles} = 195.49\ \text{grams}$$

This relationship can be used to convert moles to volume. For gasses at STP, one can refer to the standard molar volume of an ideal gas, 22.4 L for every mole. Thus, if we have 15 L of any gas at STP, we can convert to moles of substance:

$$\frac{1\ \text{mole}}{22.4\ \text{L}} \times\ 15\ \text{L} = 0.67\ \text{moles}$$

Solutions are often described in terms of molarity (M = moles/liter). Thus, if we would like to find the number of moles in 2.5 L of a 0.5 M solution:

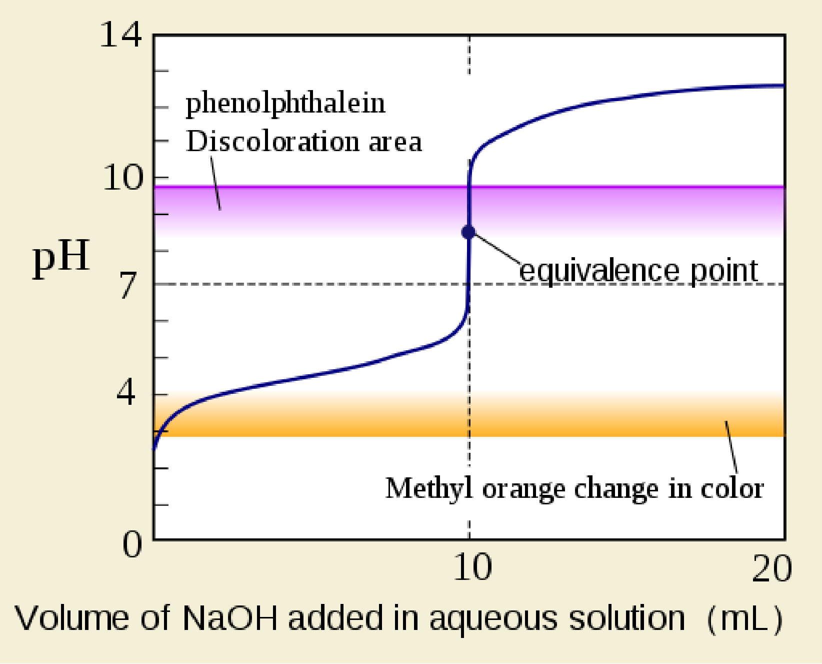
$$\frac{0.5\ \text{mole}}{1\ \text{L}} \times\ 2.5\ \text{L} = 1.25\ \text{moles}$$

The ratios of molecules in a chemical reaction can be used in a similar way to find the amount of substance involved in a reaction. For these kinds of problems, first make sure the equations are balanced. Then you can treat ratios of molecules in the reaction to relate given information to the substance needed in the answer.

Introduction to Titration

Titration is a technique used to find the concentration of a solution based on the known concentration of another solution, called the titrant. Titration is based on a chemical reaction between the two solutions that is able to come to completion, which is often marked by a measurable change like the appearance of a color or a precipitate.

The point at which the titrant neutralizes the solution is called the **equivalence point**. **Titration curves** are used to monitor the progress of the reaction by plotting the titrant added on the *x*-axis compared to the monitored change, such as change in pH or color.



Note that free response questions about titration often appear on the AP exam. Be sure that you are able to estimate the equivalence point and the concentration of the solution based on chemical equations and stoichiometry, as well as features of the titration curve.

Types of Chemical Reactions

Types of reactions are classified by the processes that produced the reaction. For the purposes of the AP exam, it is useful to be able to identify certain types of chemical reactions. **Acid-base reactions** involve the transfer of protons between chemicals. **Oxidation-reduction** reactions involve the movement of electrons between chemicals. **Precipitation reactions** involve the formation of an insoluble product, called a precipitate.

Introduction to Acid-Base Reactions

Acids and bases are defined by several theories. **Arrhenius theory** states that substances that ionize to produce protons (H^+) in water are acids and substances that produce hydroxide (OH^-) in water are bases. This theory limits acid and base definitions to those that take place in water; thus, the **Brønsted-Lowry theory** expands on this, stating that substances that donate protons are acids, and those that accept protons are bases. In Brønsted-Lowry equations, the molecule that receives the proton is called a **conjugate acid**, while the molecule that is left after donating the hydrogen ion is a **conjugate base**. Acid-base reactions will be covered in more detail in later sections.

Oxidation-Reduction (Redox) Reactions

Oxidation-reduction (redox) reactions are reactions involving a transfer of electrons between reactants. In redox reactions, there is always an **oxidized species**, whose electrons are lost, and **reduced species**, who gain electrons. This can be remembered using the mnemonic “LEO says GER” (Loss of Electron is Oxidation, Gain of Electron is Reduction).

Oxidation state or number is the number of electrons that an atom gains, loses, or uses in a reaction and can be a positive or negative integer or 0. An increase in oxidation number reflects oxidation and a decrease reflects reduction. Several rules can be used to assign oxidation numbers:

- Free atoms have an oxidation state of 0
- Hydrogen has an oxidation state of +1 (except for hydride)
- Oxygen has an oxidation state of -2 (except for peroxide)
- In a compound or ion, the oxidation state is equal to the total charge
- Fluorine, bromine, and chlorine have an oxidation state of -1, except when bound to a lighter halogen, oxygen, or nitrogen
- Group 1 metals are +1, group 2 are +2

Redox reactions occur in various forms:

- Combination reactions: $\mathrm{A + B \rightarrow AB}$
- Decomposition reactions: $\mathrm{AB \rightarrow A + B}$
- Replacement reactions: $\mathrm{AB + C \rightarrow A + BC}$
- Combustion with oxygen: $\mathrm{C_xH_y + O_2 \rightarrow CO_2 + H_2O}$

Redox reactions are balanced using two reactions called **half-reactions**:

$$\text{oxidation: } \mathrm{A \rightarrow A^+ + e^-}$$
$$\text{reduction: } \mathrm{B^+ + e^- \rightarrow B}$$
$$\text{overall: } \mathrm{B^+ + A \rightarrow B + A^+}$$

To write net ionic equations for redox reactions, both the number of atoms and the charge are balanced on both sides of the reaction. The method to do this involves sequential steps:

1. Write out the unbalanced equation.
2. Identify and assign oxidation numbers for each atom.
3. Separate out the half reactions, one with the oxidized atoms and one with reduced atoms. Include the number of electrons lost and gained on each side.

4. Multiply coefficients so that the gains and losses of electrons are balanced in the half reactions.
    a. In acidic or aqueous solutions, first balance atoms that are not H or O, then balance charge using H^+ and OH^-. Then balance oxygen using H_2O.
5. Recombine the half reactions.
6. Balance any elements whose oxidation state did not change.
7. Double-check your work by confirming that all elements and charges are balanced.

Outside Reading

- For additional information on balancing equations, see:
    - http://www.occc.edu/kmbailey/Chem1115Tutorials/Net_Ionic_Eqns.htm

- For examples of how to balance redox reactions, see:
    - https://www.periodni.com/balancing_redox_equations.php

- For more information on stoichiometery and balancing equations, see:
    - https://www.khanacademy.org/science/chemistry/chemical-reactions-stoichiome/stoichiometry-ideal/a/stoichiometry
    - https://chem.libretexts.org/Bookshelves/Inorganic_Chemistry/Supplemental_Modules_(Inorganic_Chemistry)/Chemical_Reactions/Stoichiometry_and_Balancing_Reactions

- For more information on titrations, see:
    - https://sites.google.com/a/ramapocentral.net/ap-chemistry/chapter-15-applications-of-aqueous-equilibria/ph

Sample Chemical Reactions Questions

What is the final concentration of anions when a solution is made by adding 300.0 mL of 4.0 M $MgCl_2$ to 200.0 mL of 3.0 M$NaNO_3$?

A. 0.6 M

B. 3.0 M

C. 5.0 M

D. 6.0 M

Explanation:

The correct answer is D. Anions are negative ions, and the solutions in the question will contain Cl^- and NO_3^- ions in solution. Remember that $MgCl_2$ will produce 2 moles of Cl^- and $NaNO_3$ will produce 1 mole of NO_3^-. Calculate the moles of each anion that will be present in the solution, and divide by the volume of the solution in liters to calculate the molarity.

$$(0.3000\text{ L})\left(\frac{4.0\text{ mol MgCl}_2}{1\text{ L}}\right)(2) = 2.4\text{ mol MgCl}_2$$

$$(0.2000\text{ L})\left(\frac{3.0\text{ mol NaNO}_3}{1\text{ L}}\right) = 0.60\text{ mol NaNO}_3$$

$$\frac{3.0\text{ mol anions}}{0.500\text{ L}} = 6.0\text{ M Total Anions}$$

When 2.0 g $K_2CO_{3(s)}$ was added to a beaker of 75 mL 3 M $HNO_{3(aq)}$, vigorous bubbling occurred. Which statement best explains this phenomenon?

A. Water vapor is released.

B. The solution was poured too fast.

C. $K_2CO_{3(s)}$ reacts violently when added to water

D. Carbon dioxide is released by the reaction.

Explanation:

The correct answer is D. This is a gas-evolution reaction. When carbonates and bicarbonates ($CO^2{}_3^-$ and HCO_3^-) react with acids, the gas product is CO_2. The reaction is $K_2CO_{3(s)} + 2HNO_{3(aq)} \rightarrow CO_{2(g)} + H_2O_{(l)} + 2KNO_{3(aq)}$. There is not enough energy released to boil the water.

What type of reaction best describes this process?

$$Zn^0 + Cu^{2+} \rightarrow Zn^{2+} + Cu^0$$

A. Synthesis reaction

B. Decomposition reaction

C. Redox reaction

D. Neutralization reaction

Explanation:

The correct answer is C. Redox (or oxidation–reduction) reactions involve the transfer of electrons from one reagent to the other. In this case, Zn^0 transfers two electrons to Cu^{2+} to form Zn^{2+} and Cu^0.

Kinetics

Around 7–9% of questions on the AP exam will cover Kinetics.

Reaction Rate

Kinetics is the study of **reaction rates**, the change in concentration over a given period of time:

$$\text{reaction rate} = \frac{\Delta\text{concentration}}{\Delta\text{time}}$$

Reaction rate can also be expressed in terms of the reaction constituents. Consider the reaction:

$$A + 2B \rightarrow 3C$$

The reaction rate can be expressed as any of the following:

$$\text{reaction rate} = -\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[B]}{2\Delta t} = \frac{\Delta[C]}{3\Delta t}$$

Note that as reactants decrease over time, Δ[reactants] will be negative; thus, a negative sign is added to the equation to generate a positive overall reaction rate. To account for differences in molar quantities due to the stoichiometry of the reaction, the coefficients are divided for *B* and *C* in this reaction.

The **rate constant** is determined by the **Arrhenius equation**:

$$k = Ae^{-E_a/RT}$$

A = an expression of the fraction of molecules reacting at kinetic energy of 0
E_a = activation energy (joules)
R = universal gas constant
T = temperature (Kelvin)

As shown by the equation, the rate constant is dependent on the temperature that the reaction takes place, as an increase in temperature increases the kinetic energy of a reaction up to a certain point. An increase in kinetic energy increases the chances of molecules colliding and thus reacting with each other, in turn increasing the reaction rate. This rate follows an exponential scale, meaning an increase in 10 K doubles the reaction rate.

Introduction to Rate Law

Rate law describes the relationship between reaction rate and the concentrations of reactants. Consider the reaction:

$$aA + bB \rightarrow cC$$

The rate law is expressed as:

$$\text{reaction rate} = k[A]^s[B]^t$$

Where k is the experimentally determined rate constant for the reaction at a given temperature and s and t are the reaction orders for the A and B, respectively. The **reaction order** indicates the effect of a reactant on the overall reaction. For instance, if doubling a reactant results in doubling the rate, then the reaction order for that molecule will be 1 ($[2]^1 = 2$).

If doubling a reactant causes a four-fold increase in rate, then the reaction order for that molecule is 2 ($[2]^2 = 4$). The overall reaction order is equal to the sum of the individual reaction orders of reactants:

$$\text{reaction order} = s + t$$

In practical terms, these equations mean that the concentration of reactant A decreases by a factor of s and the concentration of reactant B decreases by a factor of t. For example, given the reaction:

$$A + B \rightarrow C$$
$$\text{reaction rate} = k[A]^1[B]^1$$
$$\text{reaction order} = 1 + 1 = 2$$

In this reaction, both reactants are decreasing by a factor of 1; thus, the reaction order with respect to $A = 1$ and the reaction order with respect to $B = 1$. In cases where the reaction rate is not affected by the concentration of reactants, the reaction rate = k and the reaction order is 0.

Concentration Changes over Time

Using rate equations, one can calculate the reaction order for reactants based on their concentrations in the reaction and the effect on reaction rate, or rate of formation of C.

Once the value of the reaction orders is known, the appropriate equations can be used to determine reaction properties at specific times (t) in a reaction:

	Zero Order	First Order	Second Order
Rate law	$\text{rate} = k$	$\text{rate} = k[A]$	$\text{rate} = k[A]^2$
Integrated rate law	$[A]_t = -kt + [A]_0$	$ln[A]_t = -kt + ln[A]_0$	$\frac{1}{[A]_t} = -kt + \frac{1}{[A]_0}$
Plot to determine *k*	[A] vs t	ln[A] vs t	$\frac{1}{[A]}$ vs t
Relationship of *k* slope of plot	$\text{slope} = -k$	$\text{slope} = -k$	$\text{slope} = k$
Half-life	$\frac{[A]_0}{2k}$	$\frac{ln2}{k}$	$\frac{1}{k[A]_0}$

Half-life is the time it takes for half the reactants to convert to products. In radioactive decay, half-life demonstrates first-order kinetics and can range from milliseconds to billions of years. To determine the rate of decay (λ) given a half-life ($t_{\frac{1}{2}}$) we use the equation:

$$\lambda = \frac{ln2}{t_{\frac{1}{2}}}$$

Given the λ and the initial amount of the sample (N_0) it is possible to find the amount of a radioactive sample remaining (N_t) after a given amount of time (t), with the equation:

$$N_t = N_0 e^{-\lambda t}$$

Since half-life is constant for a given isotope, it can be used to estimate the age of an item, as is used in carbon-14 dating using the above equations.

Elementary Reactions and Reaction Mechanisms

Elementary reactions are the simplest type of reaction, involving only a single step. These are defined by the number of reactants. For example, a **unimolecular reaction** involves a single reactant. These can include isomerization of a reactant or decomposition reactions, like the decomposition of hydrogen peroxide to water and oxygen:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

In **bimolecular reactions**, two molecules react to form a product. These are the most common types of reactions that you'll come across. Reactions that involve the collision of three or more molecules at a time are extremely rare; more often, reactions that involve more than two reactants take place in a stepwise fashion and form intermediates between steps that do not show up in the final equation.

For example, take the reaction:

$$A + B \rightarrow C + D$$

The reaction takes place in two steps that, when added together, result in the overall reaction given above.

$$A \rightarrow C + E$$
$$E + B \rightarrow D$$

In these types of multi-step reactions, the reaction mechanisms are built on several elementary reaction steps; the components include reactants, intermediates, products, and catalysts. The **reaction intermediates** (*E* in the equation above) do not show up in the final products. Identifying the reaction intermediates can help you identify the mechanism of the reaction.

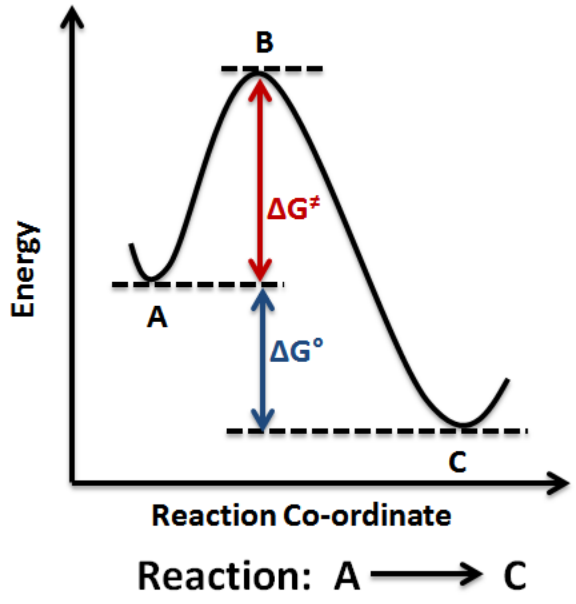
The slowest step in a multi-step reaction is referred to as the **rate-determining (or rate-limiting) step**. The rate law for the whole reaction would then be the rate of the rate-determining step. In multi-step reactions where there is no rate limiting step, the rate law is estimated through a **steady-state approximation.** The assumption for this is that there should be an intermediate that is consumed at the same rate that it is created; thus, its concentration remains constant through the reaction—this is called reaching steady state. Be sure to practice identifying the rate law for steady state reactions as well.

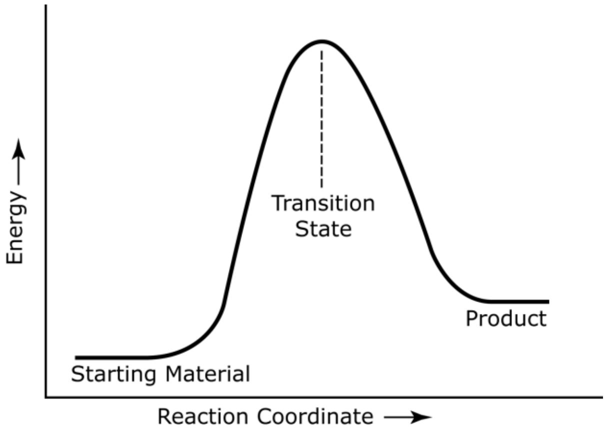
Collision Model

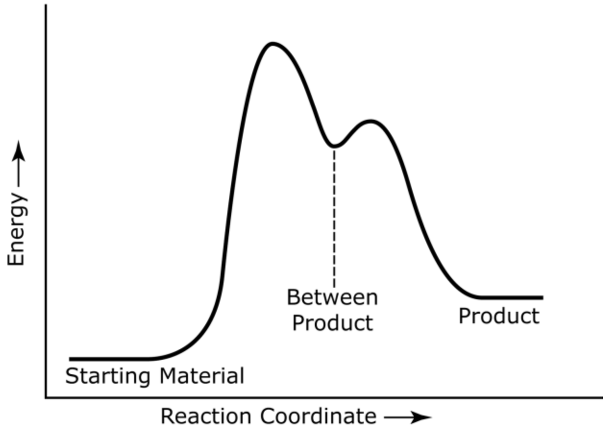
For reactions to occur, reactant molecules must collide together with enough energy to break chemical bonds and in a proper orientation to form new ones. There are several factors that alter how often these events happen, and thus affect the reaction rate including concentration of reactants, surface area of reactants, the complexity of reactant molecules, temperature, and presence of a catalyst.

Reaction Energy Profile

Reaction energy diagrams show the relationship between reaction energy (*y*-axis) and the phase of the reaction (*x*-axis). By looking at the diagram for a reaction where *A* converts to *B* via a transitional state of *C*, you should be able to quantify the activation energy (the difference in energy between *A* and *B*) as well as the energy change between reactants and products.







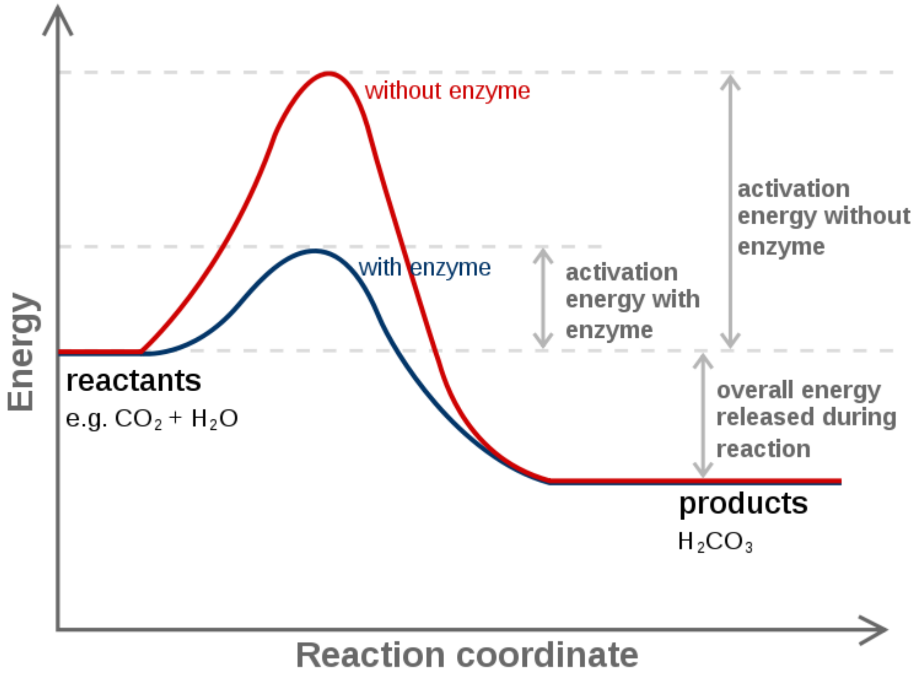
In multi-step reactions, the energy profile appears with multiple peaks, which correlate to the activation energy for each elementary reaction.

Catalysis

Activation energy can be modulated by the presence of a catalyst. **Catalysts** are molecules that lower the activation energy without actually being consumed by a reaction. In biology, catalysts are generally enzymes that put molecules in optimal configurations for reactions to proceed efficiently. When a catalyst is added to a reaction, the reaction rate becomes:

$$k = Ae^{-(E_a - \mathit{\Delta} E_a)/RT}$$

Where $\mathit{\Delta} E_a$ is the amount the activation is energy is lowered by the addition of the catalyst.



Outside Reading

- For additional information on kinetics, see:
    - https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Kinetics/Reaction_Rates/Reaction_Rate
    - https://courses.lumenlearning.com/boundless-chemistry/chapter/reaction-mechanisms/

Sample Kinetics Questions

Which of the following actions will *decrease* the rate of the reaction?

A. Lowering the temperature

B. Increasing the pressure

C. Adding a catalyst

D. Increasing [N_2] (at constant pressure)

Explanation:
The correct answer is A. Lowering the temperature decreasing the kinetic energy of the gas molecules, meaning fewer have the minimum energy necessary to react. Increasing the pressure will increase the rate at which collisions occur and will accelerate the rate of reaction. Catalysts lower the energy of activation and increase the rate of reaction. Industrially, heterogeneous iron catalysts are used to accelerate this reaction. Finally, increasing the concentration of [N_2] will shift the equilibrium towards the right, but it will not affect the rate of reaction.

The reaction of nitrogen dioxide with carbon monoxide to produce nitric oxide and carbon dioxide is a multi-step reaction. Experimental work has determined that the rate law for the equation follows the equation: rate = $k[NO_2]^2$. Which elementary reaction is most likely the rate-determining step (RDS)?
$NO_2 + CO \rightarrow NO + CO_2$

A. $2NO_2 \rightarrow NO_3 + NO$
B. $CONO_2 \rightarrow NO + CO_2$
C. $NO_2 + CO \rightarrow NO + CO_2$
D. $NO_2 \rightarrow NO + O$

Explanation:
The correct answer is A. The overall rate law reflects the rate equation that corresponds to the rate-determining step. Here, since the rate law is second order in $[NO_2]$ (rate = $k[NO_2]^2$), the RDS must involve 2 molecules of NO_2 and no other species.

If the half-life of a radioactive element is 6 minutes, which of the following was the initial mass of a sample with 40.0 grams left after 36 minutes?

A. 80 grams

B. 160 grams

C. 2,560 grams

D. 5,120 grams

Explanation:

The correct answer is C. After 36 minutes, six half-life cycles have occurred: $\frac{1}{6} \rightarrow 6 \rightarrow \frac{1}{64}$.

Unknown mass × $\frac{1}{64}$= 40 grams ∴ unknown mass = 2,560 grams

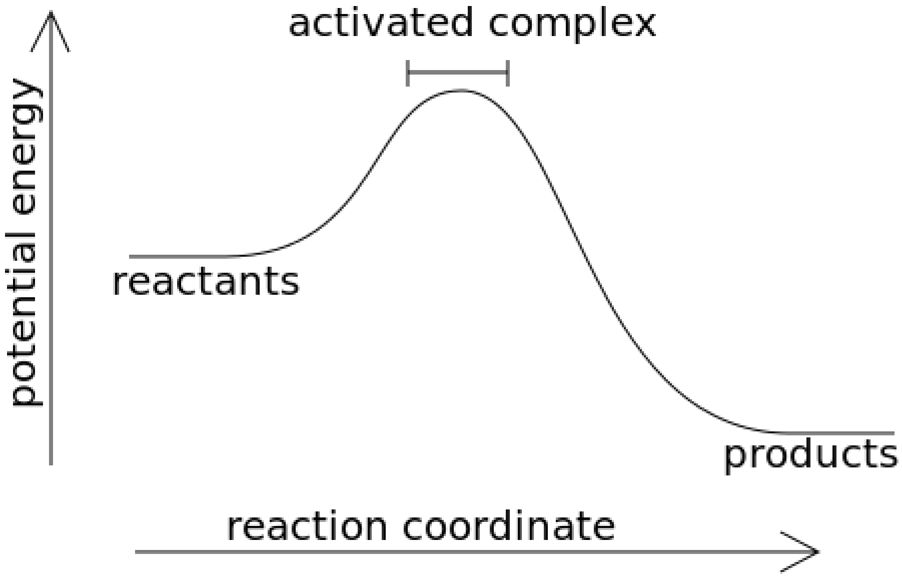
Thermodynamics

About 7–9% of the questions on your exam will cover Thermodynamics.

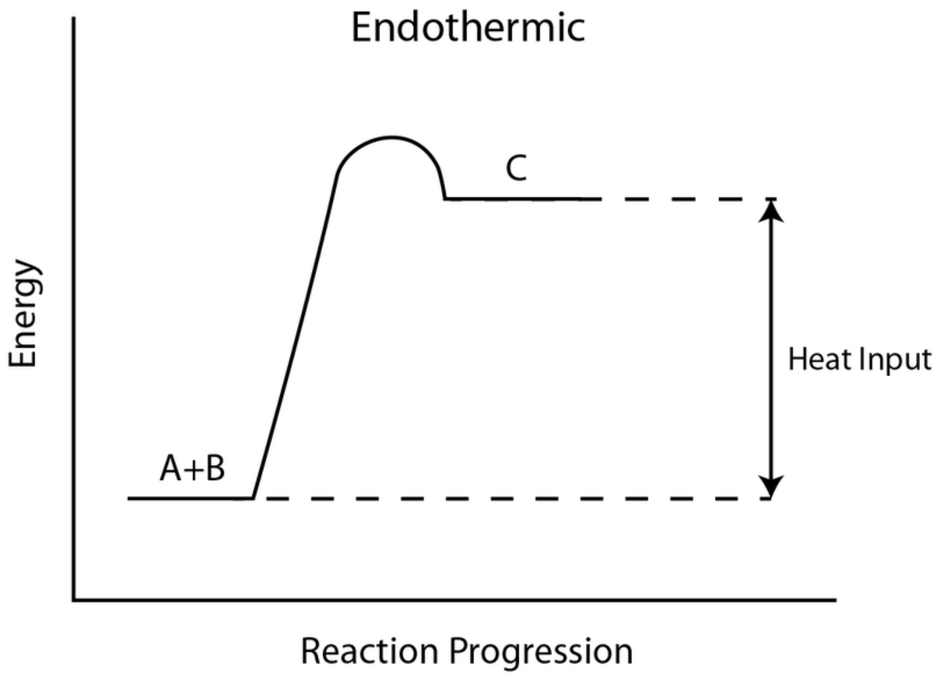
Endothermic and Exothermic Processes

Thermodynamics deals with the relationship between heat and other forms of energy. During a chemical reaction, temperature changes indicate that there has been a change in energy. These changes in energy are due to phase changes or changes in bonds.

Exothermic reactions release energy into their surroundings in the form of heat.



Endothermic reactions absorb energy from their surroundings, resulting in a drop in temperature.



The potential energy of a reaction represented in an energy diagram tells you whether the reaction is endothermic or exothermic. If potential energy is decreased in the products relative to the reactants, this represents a release of energy from the reaction to the environment indicating an exothermic reaction. If the potential energy of products is increased relative to reactants, this means energy is absorbed from the environment during the reaction, indicating an endothermic reaction. The difference in energy between reactants and products is the amount of energy absorbed or released.

Heat Transfer and Thermal Equilibrium

When two substances of different temperatures come into contact with each other, they will exchange thermal energy. The point when the two substances have uniform temperatures is **thermal equilibrium.** At thermal equilibrium, there is no net exchange of heat energy. The process of reaching thermal equilibrium can be explained through a kinetic model. The molecules in each substance have their own kinetic energy, with the warmer substance having greater kinetic energy than the cooler substance.

When the molecules of the substances come into contact with each other, the molecules begin to collide. In doing so, the molecules from the warmer substance transfer energy as heat to the molecules of the cooler substance. These molecular collisions and energy transfers continue, eventually causing both substances to have the same average kinetic energy at thermal equilibrium.

Heat Capacity and Calorimetry

The first law of thermodynamics states that energy is conserved in chemical and physical reactions. Thus, in a closed system the change in energy is equal to the energy supplied minus the work done on its surroundings. This means that heat is not created or destroyed, but rather transferred between systems. Energy changes in a system occur in the form of heat, phase transitions, and chemical reactions.

Warmer systems transfer energy as heat to cooler systems. The amount of heat transferred (*q*) between the systems is expressed using the following equation:

$$q = mc\Delta\mathrm{T}$$

where *m* is the mass, *c* is the **heat capacity** (the amount of heat needed to change the temperature by 1°), and *ΔT* is change in temperature. It is important to note that the temperatures of different substances of the same mass with the same amount of energy transferred may not have equivalent temperature changes. This is due to differences in the heat capacity (*c*) of the substances. Heat capacity is expressed as specific heat capacity or molar heat capacity, the amount of heat needed to change the temperature of 1 gram or 1 mole of substance by 1 degree, respectively.

Calorimetry is used to measure heat in a reaction by measuring how much heat is absorbed or produced by a reaction. **Coffee cup calorimeters** measure the heat given off in the form of water according to the equation:

$$\Delta H_{\mathrm{reaction}} = -\mathrm{mc}\Delta T$$

Bomb calorimeters, on the other hand, use materials other than water to measure the change in heat. These rely on changes in **heat capacity**, the amount of heat needed to change the temperature by 1°. Bomb calorimeters follow the equation:

$$\Delta H_{\mathrm{reaction}} = -C\Delta T$$

where *C* is the heat capacity of the calorimeter in J/°*C*.

Energy of Phase Changes

Energy transfer must occur for phase changes to take place. The energy of a system increases to go from solid, to liquid, to gas. An equivalent amount of energy is released during a phase change in the reverse direction (gas to liquid to solid). The **heat of fusion (ΔH_f)** is the amount of energy needed for a unit of substance to change from solid to liquid. This same amount of energy is released when liquid turns into a solid. The **heat of vaporization (ΔH_v)** is the energy needed for a substance to go from liquid to gas. Again, the same amount of energy is released when a substance condenses from gas to liquid. The heat (***q***) required for a phase change is dependent on the number or moles of substance (***n***). For example, the amount of energy needed for a substance to go from solid to liquid is determined by the equation:

$$q = \mathrm{n}\,\Delta H_f$$

Enthalpy of Reaction

Enthalpy refers to the energy of a system, usually expressed as heat. It is equal to the internal energy of a system, plus the product of pressure and volume of the system. For the sake of the AP exam, pressure and volume is held constant, so enthalpy can be thought of as equivalent to the energy of the system.

The enthalpy change of reaction (ΔH) is equivalent to the amount of energy released (negative ΔH) or absorbed (positive ΔH). The enthalpy of reaction is the difference between enthalpy of products vs. reactants.

$$\Delta H_{\text{reaction}} = H_{\text{products}} - H_{\text{reactants}}$$

This is expressed in kJ/mol, and under standard conditions (constant pressure and volume), is related to the number of moles of reactants. Thus, the enthalpy of reaction is scalable based on the amount of reactants in an equation. For example, in the equation:

$$2\mathrm{A} + \mathrm{B} \rightarrow \mathrm{A_2B} + 500\ \mathrm{kJ}$$

The overall enthalpy of reaction would be –500 kJ, as 500 kJ of energy was released. If you double the reactants (4 moles of A and 2 moles of B), the enthalpy or reaction becomes –1,000 kJ.

Bond enthalpy is the amount of energy needed to break one mole of a bond. Bond breaking is always endothermic, as it requires absorbing energy. Bond making, on the other hand, is always an exothermic process, as it requires releasing energy. The amount of energy needed in a reaction is estimated by adding up the average energies of each bond in the reaction. Remember that the sign for bond formation is negative, as there is a release of energy.

For example, in the above reaction, we can see that 500 kJ is released by the formation of A_2B. Given that this chemical reaction does not break any bonds, and only forms 2 A-B bonds, we can calculate that the bond enthalpy of A-B is 250 kJ.

Enthalpy of Formation

The standard **heat of formation (ΔH°_f)** is the change in enthalpy that occurs when one mole of a substance is formed from its pure elements under standard conditions. The ΔH°_f for a reaction is equal to the sum of ΔH°_f for products minus the sum of ΔH°_f for reactants:

$$\Delta H^\circ{}_{\text{reaction}} = \Sigma \Delta H_f{}^{o}{}_{\text{products}} - \Sigma \Delta H_f{}^{\circ}{}_{\text{reactants}}$$

In other words, given the reaction between chemical A and B to form C:

$$\mathrm{A} + \mathrm{B} \leftrightharpoons \mathrm{C}$$

The enthalpy of the formation would be:

$$\Delta H^\circ{}_{\text{reaction}} = \Delta H_f{}^{\circ}{}_{\mathrm{C}} - (\Delta H_f{}^{\circ}{}_{\mathrm{A}} + \Delta H_f{}^{\circ}{}_{\mathrm{B}})$$

Hess's Law

In complicated reactions with multiple states, the heat of the reaction is measured by the sum of the heats of individual reactions. This is called **Hess's Law**. Remember that when the reaction moves in the opposite direction, the heat of reaction is the same in magnitude, but the sign changes (i.e., it is endothermic in one direction and exothermic in the other).

This concept can be extended to measure the heat of state changes as the product of the final state minus the initial state. **Heat of vaporization**, for example, is the heat required for a liquid to turn into a vapor:

$$\Delta H_{\text{vaporization}} = H_{\text{vapor}} - H_{\text{liquid}}$$

Outside Reading

- For more information on energy in phase changes, see:
    - https://chem.libretexts.org/Courses/can/health/07%3A_Energy_and_Chemical_Processes/7.4%3A_Phase_Changes

- For more on reaction enthalpy, see:
    - https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/05._Thermochemistry/5.4%3A_Enthalpy_of_Reaction

Sample Thermodynamics Questions

Which of the following is a true statement about an endothermic reaction?

A. It releases heat.

B. Increasing the temperature shifts the equilibrium towards the products.

C. It is thermodynamically favored at all temperatures.

D. The use of a catalyst slows the reaction rate.

Explanation:

The correct answer is B. In an endothermic reaction, heat can be thought of as a reagent in the chemical equation. By increasing the temperature (adding heat), the equilibrium is shifted towards formation of products. Exothermic reactions release heat, while endothermic reactions absorb heat from their surroundings. For a reaction to be spontaneous, the free energy ($\Delta G = \Delta H - T\Delta S$) must be negative. In an endothermic reaction $\Delta H > 0$, so in order to be spontaneous, ΔS must be positive and the reaction must be done at a high enough temperature such that $T\Delta S > \Delta H$. Finally, the use of a catalyst will always accelerate the rate of reaction.

Species	ΔH_f^0 (kJ/mol)
Al_2O_3	−1,670
Fe_2O_3	−826
SO_2	−297
TiO_2	−945
MnO	−385
MnO_2	−520

The standard enthalpies of formation of several oxides are listed in the table above. Based on the data in the table, which metal oxide has the strongest average metal-oxygen bond?

A. Al_2O_3
B. SO_2
C. TiO_2
D. MnO

Explanation:

The correct answer is C. The strength of the metal–oxygen bond is proportional to the energy released in its formation. TiO_2 has an enthalpy of −945 kJ/mol. This is divided over 2 Ti–O bonds, giving an average bond enthalpy of −473 kJ/mol.

A 100-gram aluminum block is heated to 100°C and placed in an insulated vessel containing 100 grams of ice-cold water (0°C). After the system is allowed to reach thermal equilibrium, the temperature of the water was recorded as 20°C. What is the magnitude of the specific heat capacity of water compared to the specific heat capacity of aluminum?

A. The specific heat capacity of water is 4 times less than the specific heat capacity of aluminum.
B. The specific heat capacity of water is 5 times less than the specific heat capacity of aluminum.
C. The specific heat capacity of water is 4 times greater than the specific heat capacity of aluminum.
D. The specific heat capacity of water is 5 times greater than the specific heat capacity of aluminum.

Explanation:

The correct answer is C. The energy lost from the Al block must be equal to the energy gained by the water. The energy lost by the Al block is equal to the change in temperature multiplied by the heat capacity (C) of Al: ($\Delta T \times C_{Al}$). Likewise, the energy gained by the water is: ($\Delta T \times C_{H2}O$). Setting these equations equal we have:

$$(80\ ^\circ C \times C_{Al}) = (20\ ^\circ C \times C_{H2}O)$$

Rearranging, we have:

$$\frac{C_{H_2O}}{C_{AI}} = \frac{80^\circ C}{20^\circ C} = 4$$

The heat capacity of water is 4 times greater than that of Al.

Equilibrium

Around 7–9% of questions on your AP exam will cover Equilibrium.

Introduction to Equilibrium

Most reactions do not proceed to completion; rather, while the reactants make products a reverse reaction occurs wherein the products convert back to reactants. This sort of reaction is represented with a chemical equation with both forward and reverse arrows:

$$aA + bB \rightleftharpoons cC + dD$$

As the reactions proceed, the reaction rates become equal, called **chemical equilibrium**. When a reaction has reached chemical equilibrium, chemical concentrations in the reaction (A, B, C, and D) are steady. This state is also referred to as **dynamic equilibrium**. In this state, reactions continue to occur to generate reactants and products, but there is no net change in the ratios. On the contrary, **static equilibrium** refers to a state where the reaction is completed and there is no conversion occurring between products and reactants.

To identify if a reaction is moving in the **forward direction** (reactants converting to products) or the **reverse direction** (products converting to reactants), one can look at the rate of reaction for each reaction. If the reaction rate of the forward reaction is greater than reverse, then that is the preferred reaction and the conversion to products will be favored. If the reaction rate of the reverse reaction is higher, then there will be a greater conversion of products to reactants.

Reaction Quotient and Equilibrium Constant

The **equilibrium constant (*K_c* or *K_{eq}*)** is the ratio of product concentrations divided by reactant concentrations, each raised to their respective stoichiometric coefficients. For the equation:

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

$$K_c = \frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b}$$

When calculating the equilibrium constant, remember that pure solids and pure liquids are generally not included in the calculation. To get the correct K_c, make sure the equation is first balanced, and that the coefficients are reduced to the lowest integers. In processes that have multiple steps, K_c is equal to the product of the K_c of each step. K_c is constant for a reaction at set temperature and pressure. If these variables change, then the K_c will change as well.

Reactions that have not reached equilibrium have a similar expression, called a **reaction quotient (*Q*)**. When a reaction has reached equilibrium, *Q* is equal to K_C. Comparison of K_C and *Q* can be used to determine whether a reaction is at equilibrium. For example, if *Q* is less than K_c, the reaction has not yet reached equilibrium and will favor products. If *Q* is higher than K_c, the reaction will favor reactants. K_c can also tell us whether reactants or products are favored at equilibrium. A K_c of more than 1 favors products while a K_c less than 1 favors reactants. The magnitude of the number tells how strongly the reactants or products are favored. For example, a K_c of 1.5 has slightly more products than reactants. A K_c of 1,000 would be mostly products and very little reactants.

For gasses, the equilibrium constant can be expressed in either mol/L (K_c) or in pressure units (K_p). The K_p calculation only takes into account molecules that are in the gas phase and is calculated using a similar equation as K_c, where pressures are substituted for concentrations. To convert between K_c and K_p, a modified version of the ideal gas law is used:

$$K_p = K_c(\mathrm{RT})^{\Delta \mathrm{n}}$$

$$\Delta n = \text{mol of product gasses} - \text{mol of reactant gasses}$$

Calculating Equilibrium Concentrations

Equilibrium constant is used to calculate the concentration of products or reactants. For the AP exam, use a RICE table to calculate unknown concentrations. Remember that RICE stands for Reaction, Initial concentrations, Change, Equilibrium concentrations, which is the format of the table. Imagine you are given the formula:

$$aA + bB \rightleftharpoons cC$$

To fill in a RICE table, first fill in reaction components, then fill in the concentrations of initial reaction components given, then calculate the expected change in reaction based on the stochiometric equation. This will then allow you to fill in the equilibrium concentrations based on the initial concentrations and change. For example, if you know that at the beginning of the reaction molarities of A and B are both 1 and C is not present then at equilibrium the molarity of C is 0.5, and you can then fill in the table accordingly:

Reaction	*aA*	*bB*	*cC*
Initial Concentrations (M)	1	1	0
Change	–*ax*	–*bx*	+*cx*
Equilibrium Concentrations (M)	1–*ax*	1–*bx*	0.5 = 0+*cx*

The concentrations of reactants are both known to be 1 M while *c* is not present, so a molarity of 0 is a given. As reactants are converted to product in the reaction, the changes in reactants are both negative and the change in product is positive. The stochiometric coefficients determine the magnitude of the reaction. The unknown change in reaction is denoted by the term *x*. The equilibrium concentrations are then determined by writing out the sums of initial concentration and the change. As the equilibrium concentration of *C* is given, you can then solve for *x* to find the equilibrium concentrations of the reactants in this case it would be:

$$x = \frac{0.5\ \mathrm{s}}{c}$$

Note that on the free response section, you may be asked to determine the equilibrium concentrations and then determine the equilibrium constant based on these values.

Introduction to Le Châtelier's Principle

LeChâtelier's principle asserts that when a change in pressure, temperature, or concentration of molecules (products or reactants) are applied to a system at equilibrium, the reaction will shift to re-establish equilibrium. In other words, when there is a change in the system that disrupts the balance between *Q* and *K*, then the reaction will shift to bring these back to equality by changing concentrations or partial pressures.

- *Pressure* increases favor fewer moles of gas. For example, increasing pressure in a reaction that involves gas dissolving into liquid causes more of the gas to stay dissolved in liquid and lowering pressure favors gas to be released from the liquid. Think of how opening a bottle of soda releases pressure and dissolved carbon dioxide quickly bubbles out of solution.
- *Temperature* increases cause the reaction to shift to use the heat. To determine which way the reaction will move, you will need to know whether the reaction is exothermic or endothermic. Adding heat to an exothermic reaction will shift towards the reactants to balance the temperature change. Adding heat to an endothermic reaction will shift towards the products. Note that changing temperature changes the *K* of a reaction, not *Q*.
- Changing the *concentration* of products or reactants causes a compensatory change to the opposite side of the reaction. Adding products increases reactants and adding reactants increases products. Note that a change in concentration causes a change in *Q* but not *K*.
- Adding *catalysts* does nothing to a system at equilibrium. The catalyst only serves to change the rate of the reaction, not to change the balance between reactants and products.

Introduction to Solubility Equilibria

The solubility product constant (K_{sp}) refers to the equilibrium constant for a solid that is dissolved in a solute. This represents the amount of solid that is able to dissolve. The higher the K_{sp}, the more soluble the substance. When calculating K_{sp}, remember that solids are not taken into account and neither is solute, so for the dissolution reaction:

$$aA_{(s)} \rightleftharpoons bB_{(aq)} + cC_{(aq)}$$

$$K_{sp} = [B]^b[C]^c$$

A solution is considered saturated when $Q = K_{sp}$. When Q is less than K_{sp}, a solid will dissolve in solute, if Q is greater than K_{sp}, the reaction is saturated and any ionic solid will precipitate.

Common-Ion Effect

The **common ion effect** occurs when an ion is shared between two equilibria. For example, imagine mixing a solution of KCl and NaCl; Cl^- is shared between two ions. The solubility is measured to account for the different concentration of each ion in solution. Thus, the solubility constant would be calculated as:

$$K_{sp} = [\mathrm{K}^+][\mathrm{Na}^+][\mathrm{Cl}^-]^2$$

If KCl is added to a saturated solution of NaCl that was in equilibrium:

$$\mathrm{NaCl}_{(s)} \rightleftharpoons \mathrm{Na}_{(aq)} + \mathrm{Cl}_{(aq)}$$

The extra chloride ions would decrease the solubility of NaCl in solution, and thus shift equilibrium to favor the production of reactants.

pH and Solubility

When one of the molecules in a reaction is a weak acid or base, the pH of the solution can affect solubility. Decreasing the pH acidifies the environment and increases the solubility of weak bases, while increasing the pH reduces the solubility. The effect is the opposite in the presence of weak acids. You will not be asked to calculate solubility based on pH for the AP exam, but you may be asked to identify qualitative changes of pH based on LeChâtelier's principle.

Free Energy of Dissolution

When a molecule, like salt, dissolves in solution there is a change in energy ($\Delta G°$) due to changes in bonds and phases. This is called the **energy of dissolution**. When some salts, like sodium chloride, dissolve in water the overall change in temperature is negative. When others, like magnesium chloride, dissolve there is an increase in temperature. This can be explained due to factors like breaking of intermolecular bonds, interaction between solvent and dissolved solute, and changes in the structure of solvent around the solute. The sum of these changes can theoretically be used to estimate the energy of dissolution; however, for the sake of the exam you will only be required to explain these changes qualitatively.

Outside Reading

- For additional information on equilibrium:
    - https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Principles_of_Modern_Chemistry_(Oxtoby_et_al.)/UNIT_4%3A_EQUILIBRIUM_IN_CHEMICAL_REACTIONS

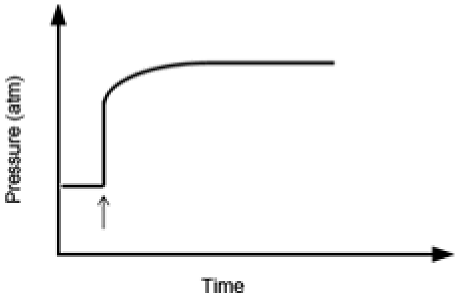
- For additional information on RICE tables, see:
    - https://www.ausetute.com.au/ricetable.html

- For more information on free energy of dissolution:
    - https://chem.libretexts.org/Bookshelves/General_Chemistry/Book%3A_CLUE_(Cooper_and_Klymkowsky)/6%3A_Solutions/6.4%3A_Gibbs_Energy_and_Solubility

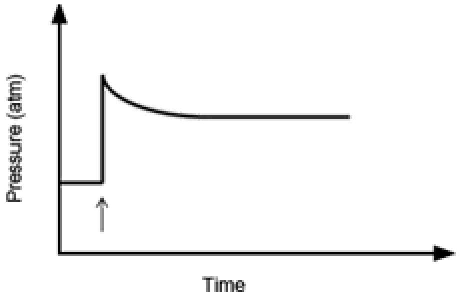
Sample Equilibrium Questions

After the system has reached equilibrium, if a quantity of NH_3 is rapidly introduced to the system, which diagram best describes how pressure will change over time (arrow indicates time gas was injected)?

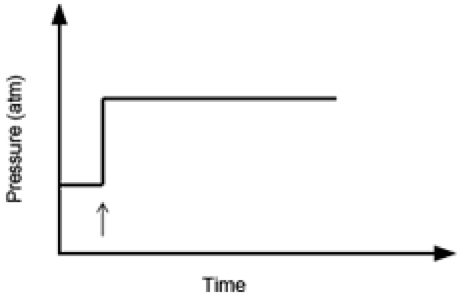
A.



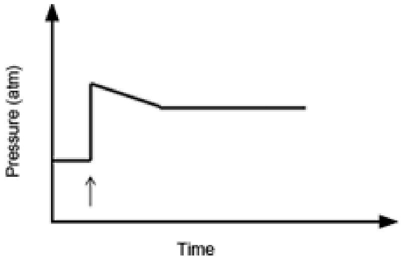
B.



C.



D.



Explanation:

The correct answer is A. Introducing NH_3 to the mixture will cause an initial rise in pressure and move the system out of equilibrium. To move back into equilibrium, some of the added ammonia will be converted back to N_2 and H_2, leading to a further increase in pressure. This is because 3 moles of H_2 and 1 mole of N_2 are produced for every 2 moles of NH_3.

The following reaction is in equilibrium at pressure *P* and temperature *T*. Which of the following changes to the reaction conditions would favor the product?

$$CO_{(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(g)} \quad \Delta H = -128.1 \text{ kJ/mol}$$

A. Decrease *P* while keeping *T* constant.
B. Decrease *T* while keeping *P* constant.
C. Remove some hydrogen gas from the container without changing *P* and *T*.
D. The reaction is always in equilibrium.

Explanation:

The correct answer is B. The reaction is exothermic according to the negative heat of reaction, ΔH, so decreasing the temperature will force the reaction to move in the direction to release more heat, towards the product side.

Which of the following is NOT considered a biologically relevant, reversible chemical reaction?

A. Hemoglobin transports oxygen by binding it in the lungs and then releasing it in cells

B. Sugar and O_2 are converted into H_2O and CO_2, which is expelled from the body

C. Nicotine from a cigarette binds receptors in the brain, giving a temporary high

D. The synthesis of ATP from ADP to store energy and the decomposition of ATP to ADP to provide energy for chemical reactions

Explanation:

The correct answer is B. The oxidation of sugar to CO_2 is an irreversible reaction. This process is highly exergonic, a common trait of irreversible reactions. Choice A is incorrect because the binding and release of O_2 by hemoglobin is a reversible process; if the reaction were irreversible, O_2 would bind permanently and could not be used in biological processes. Choice C is incorrect because the binding and release of O_2 by hemoglobin is a reversible process; if the reaction were irreversible, O_2 would bind permanently and could not be used in biological processes. Choice D is incorrect because ATP is a higher energy molecule that transfers chemical energy to other biological devices by decomposing to ADP; ADP is regenerated in living systems back to ATP and the process is repeated.

Acids and Bases

About 11–15% of all questions on your exam will cover Acids and Bases.

Introduction to Acids and Bases

Acids and bases dissociate in water in equilibrium reactions. The strength of an acid or base is related to the equilibrium constant of a reaction (K_a and K_b, respectively), where higher equilibrium constants indicate stronger acids or bases and more dissociation. The strength of an acid or base is expressed as pH or pOH respectively. **pH** represents the concentration of hydronium ions (H_3O^+, often used interchangeably with hydrogen ions H^+) in solution by the equation:

$$\mathrm{pH} = -\log[\mathrm{H_3O^+}]$$

pOH is related to the concentration of hydroxide ions (OH^-) in solution, calculated by the equation:

$$\mathrm{pOH} = -\log[\mathrm{OH^-}]$$

Water is **amphoteric**, meaning it can act as either an acid or base. Pure water autoionizes according to the equation:

$$2\mathrm{H_2O}_{(l)} \rightleftharpoons \mathrm{H_3O}^+_{(aq)} + \mathrm{OH}^-_{(aq)}$$

The equilibrium constant for this reaction is written as:

$$K_w = [\mathrm{H_3O^+}]\,[\mathrm{OH^-}] = 1.0 \times 10^{-14} \text{ at } 25°\mathrm{C}$$

Remember that the equilibrium constant is dependent on temperature, thus the K_w will change if the temperature deviates from 25° C. In neutral water, the concentrations of hydronium and hydroxide are equal; thus, pH and pOH are equal at 7.

$$pK_w = 14 = p\mathrm{H} + p\mathrm{OH} \text{ at } 25°\mathrm{C}$$

The pH scale is logarithmic, and ranges from 0 (strong acids) to 14 (strong bases). At 25°C, 7 is a neutral pH. In aqueous solutions at 25°C, you can convert between pH and pOH using the K_w or pK_w equations.

pH and pOH of Strong Acids and Bases

Strong acids dissociate completely in water. This means that the concentration of hydronium or hydroxide ions is equal to the initial concentration of the strong acid or base. Thus, the pH or pOH can easily be calculated. For example, the strong acid HCl:

$$\mathrm{pH} = -\log[\mathrm{HCl}]$$

For the exam, it is important to be able to spot common strong acids (HCl, HBr, HI, HNO_3, $HClO_4$, H_2SO_4). Strong bases to remember are hydroxides of alkali earth metals (NaOH, KOH, LiOH, CsOH, and RbOH), as well as alkaline earth metal hydroxides ($Sr(OH)_2$, $Be(OH)_2$, $Ca(OH)_2$).

A way to determine the strength of an acid or base is to consider the structure of the molecule. For example, strong acids tend to be composed of protons bound to a highly electronegative ion. This causes the electrons to concentrate around the electronegative atom, thus making the hydrogen ion more easily donated. Another factor is the strength of the bond. The stronger the H-A bond, the less likely the H^+ ion will be donated, making for a weaker acid.

Weak Acid and Base Equilibria

Weak acids and bases only partially dissociate in water with equilibrium constants below 1. Another way to express the strength of an acid is through **p*K*$_a$**:

$$\mathrm{p}K_a = -\log K_a$$

Low pK_a indicates a strong acid, high pK_a indicates a weak acid. As pH for Brønsted-Lowry acids are calculated using the dissociation of H_3O^+, we can then use the equilibrium constant to calculate the pH of a weak acid or base in solution given the molarity. To calculate pH of a weak acid (HA), first write out the balanced equation for dissociation in water:

$$\mathrm{HA}_{(aq)} + \mathrm{H_2O}_{(aq)} \rightleftharpoons \mathrm{A}^-_{(aq)} + \mathrm{H_3O}_{(aq)}$$

Note that since water is ignored in calculating equilibrium constants the equilibrium constant equation for this acid will be:

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}]}$$

If we are given the initial molarity, (Y), we can assume for any amount of weak acid that dissociates (X), the same amount of proton and weak base will form; thus, we can calculate:

	$HA_{(aq)}$ ⇌	**A^- +**	**H_3O^+**
Before equilibrium:	Y	0	0
After equilibrium:	Y – X	X	X

Then the equilibrium constant becomes:

$$K_a = \frac{[\mathrm{X}][\mathrm{X}]}{[\mathrm{Y}-\mathrm{X}]} = \frac{[\mathrm{X}]^2}{[\mathrm{Y}-\mathrm{X}]}$$

As we know this is a weak acid, and thus there is a tiny amount of dissociation compared to the initial acid, we can disregard the change in [HA] and simplify the equation further:

$$K_a = \frac{[\mathrm{X}]^2}{[\mathrm{Y}]}$$

We then solve for X, as this is the concentration of dissociated protons:

$$\mathrm{X} = \sqrt{\frac{K_a}{\mathrm{Y}}} = [\mathrm{H_3O^+}]$$

We can then put this into the equation for pH to estimate pH of the weak acid:

$$\mathrm{pH} = -\log\sqrt{\frac{K_a}{\mathrm{Y}}}$$

The same process can be used for bases by calculating the concentration of OH^-.

Acid-Base Reactions

In acid-base reactions, the pH of the resulting solution is dependent on the strength and concentration of acids and bases involved.

In a **strong acid-strong base** reaction, the reaction will proceed according to the equation:

$$\mathrm{H}^+_{(aq)} + \mathrm{OH}^-_{(aq)} \rightarrow \mathrm{H_2O_{(l)}}$$

Thus, the pH of the solution is calculated using the concentration of excess acid or base.

In a **weak acid-strong base** reaction, the equation is represented as:

$$\mathrm{HA}_{(aq)} + \mathrm{OH}^-_{(aq)} \rightleftharpoons \mathrm{A}^-_{(aq)} + \mathrm{H_2O}_{(l)}$$

If the strong base is in excess, the pH is determined by the moles of excess hydroxide ions in the solution. If the weak acid is in excess, then a buffer is created and the Henderson-Hasselbalch equation is used to determine pH (see section on buffers). If acid and base are equimolar, then the equilibrium concentrations are used to calculate the pH according to the written equilibrium reaction.

Strong acid-weak base reactions follow a similar logic as weak acid-strong base reactions. If the weak base is in excess, a buffer is created, and the Henderson-Hasselbalch equation is used. If the strong acid is in excess, then the moles of excess acid are used to determine pH. Again, if acid and base are equimolar, than the equilibrium reaction concentrations are used to determine the pH.

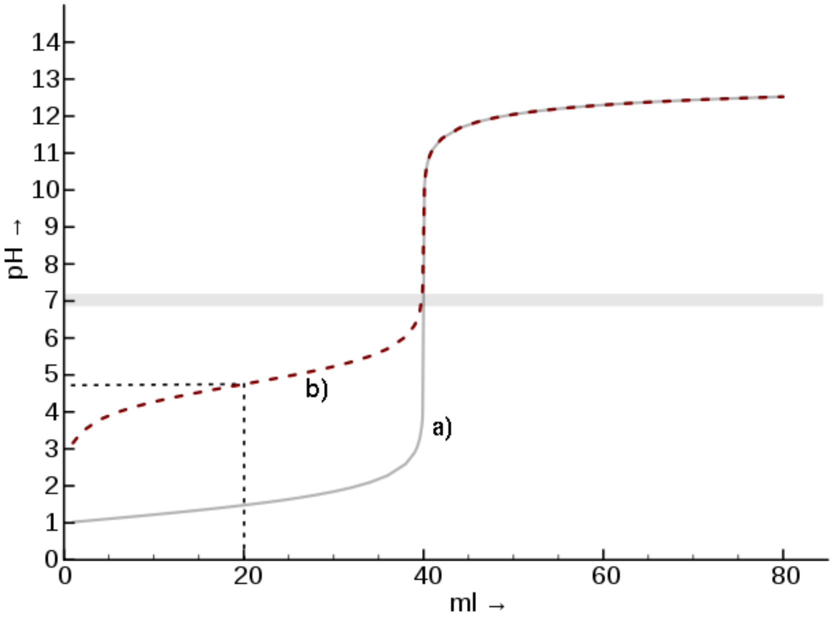
In **weak acid-weak base reactions**, the reaction will reach equilibrium, which is represented by the equation:

$$\mathrm{HA}_{(aq)} + \mathrm{B}_{(aq)} \rightleftharpoons \mathrm{A}^{-}_{(aq)} + \mathrm{HB}^{+}_{(aq)}$$

Acid-Base Titrations

A **titration curve** for an acid-base reaction plots the pH against the amount of titrant added. At the **equivalence point**, the number of moles of titrant is equal to the number of moles of analyte. The concentration and volume of titrant is then used to determine the concentration of analyte. In strong acid-strong base reactions, the equivalence point is a neutral pH (pH = 7 at 25ºC). This point is identified on the titration curve as the point where there is a sharp rise or drop in pH.

For titrations involving weak acids or weak bases, this relationship is more complicated because of the larger buffering capacity. It is useful to identify the **half-equivalence point**. At this point there are equal concentrations of the conjugate acid-base pair. When conjugate acid-base pairs have equal concentrations, pH is equal to pK_a; thus, the concentration of titrant added at this point can be used to determine concentration.



This shows two titration curves with a base as titrant and acid as analyte. Both curves have an equivalence point of 40. The grey curve shows a strong acid-base reaction with a sharp rise in pH. The red dotted curve shows a weak acid reaction with a long buffering region. In this case, the half-equivalence point, at 20, is used to determine species concentration.

For **polyprotic** acids (acids with more than one proton to donate), titration curves can be used to determine the number of protons present in the analyte. In this case, multiple equivalence points can be identified in the titration curve, each corresponding to the number of acidic protons present. You will not be asked to determine the concentration of species from titration curves of polyprotic acids, but you may be asked to qualitatively describe the major species present at points along the curve.

pH and pK_a

The pK_a of a molecule can be thought of as the pH at which the molecule will accept or donate a proton. While pH is dependent on the concentration of a solution, the pK_a is a more stable value that is unaffected by concentration. The relationship between pH of a solution and pK_a of the acid in solution can be used to determine the protonation state of acid or base in the solution. When pH < pK_a, the acid form has a higher concentration than the base form. When pH > pK_a, the base form has a higher concentration than the acid form.

Properties of Buffers

Buffers are solutions containing large amounts of a conjugate acid base or a weak pair. Buffers resist changes in pH when small amounts of acid or base are added by creating water. The conjugate acid reacts with added base while the conjugate base reacts with added acid. The pH of a buffer can be approximated using the Henderson-Hasselbalch equation for an acid (HA) and its conjugate base (A^-):

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[A^-]}{[HA]}$$

Maximum buffering capacity is reached when pH=pK_a.

Buffering capacity can be increased by increasing the concentrations of buffer components but keeping the ratios constant. By changing the ratios of conjugate acid or base, the buffering capacity changes for base or acid. For instance, increasing the amount of conjugate acid relative to conjugate base increases the buffering capacity for acid compared to base.

Outside Reading

- For further reading on acid base structure and strength, see:
    - https://chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_General_Chemistry_(Petrucci_et_al.)/16%3A_Acids_and_Bases/16.8%3A_Molecular_Structure_and_Acid-Base_Behavior

- For more reading on pH and acids and bases:
    - https://www.khanacademy.org/science/chemistry/acids-and-bases-topic#acids-and-bases

Sample Acids and Bases Questions

What is the expected result when $Ba(OH)_2$ and CH_3COOH are combined in stoichiometric amounts in aqueous solution?

$$Ba(OH)_{2(aq)} + 2CH_3COOH_{(aq)} \rightarrow$$

A. solution of pH > 7

B. solution of pH = 7

C. solution of pH < 7

D. no reaction occurs

Explanation:
The correct answer is A. Recognize that this is an acid-base reaction—CH_3COOH is acetic acid, a weak acid, which can be written as $HC_2H_3O_2$. Barium hydroxide is a strong base. When the reaction is balanced the acid and base form a solution of water and a salt, which remains dissolved in solution:

$$Ba(OH)_{2(aq)} + 2CH_3COOH_{(aq)} \rightarrow 2H_2O_{(l)} + Ba(C_2H_3O_2)_{2(aq)}$$

The salt of a weak acid and a strong base is a basic salt, which will, through hydrolysis, make the solution at the equivalence point basic.

Which of the following aqueous solutions will be basic and act as a buffer? Assume the solutions contain 1:1 mole ratios and all concentrations are 0.10 M.

A. methylamine (CH_3NH_2) and methylammonium chloride (CH_3NH_3Cl)

B. hydrofluoric acid (HF) and sodium fluoride (NaF)

C. potassium hydroxide (KOH) and hydrobromic acid (HBr)

D. sodium hydroxide (NaOH) and ammonia (NH3)

Explanation:
The correct answer is A. A basic buffer is a solution made from a weak base and its conjugate acid. Adding a strong acid or base to a buffer solution does not change the pH significantly; these solutions are used when a constant pH is desired, in this case a pH > 7.

A stock solution of an acid has a concentration of 0.15 M at STP. What is the pH of the acid?

A. 0.15

B. 12.5

C. 0.8

D. –0.15

Explanation:
The correct answer is C. The concentration of the acid is .15 M. The pH of an acid is the negative logarithm of the hydrogen-ion concentration. Thus, $\mathrm{pH} = -\log\left[\mathrm{H}^+\right]$, i.e., $\mathrm{pH} = -\log\left[0.15\right] = 0.8$.

Applications of Thermodynamics

Finally, 7–9% of the question on your exam will cover Applications of Thermodynamics.

Introduction to Entropy

Entropy is a measure of the amount of energy in a system that is not available to do work. This can also be thought of as the amount of disorder in a system. The **second law of thermodynamics** states that the universe moves in the direction of increased entropy over time. This can also be thought of as meaning that spontaneous processes move in the direction of increased entropy.

As matter in a system becomes more dispersed, the entropy increases. For example, when the state of matter changes from solid to liquid to gas, molecules become more dispersed. In this case, the entropy of the system increases as there is less available energy to do work. If you then take the gas phase and increase the volume of the container while keeping temperature constant, the entropy will further increase as the molecules move further apart. If you instead condense the gas to a liquid, the entropy of that system will decrease. Entropy also increases when energy becomes more dispersed. Kinetic energy distribution increases when the temperature increases; thus, if you increase the temperature of a system containing gas, kinetic energy becomes more dispersed, resulting in an increase in entropy.

The change in entropy of the system is calculated as:

$$\Delta S_{\text{system}} = \Sigma S_{\text{products}} - \Sigma S_{\text{reactants}}$$

Gibbs Free Energy and Thermodynamic Favorability

Gibbs free energy (G) is used to determine the thermodynamic favorability of a process. The Gibbs free energy equation takes into account changes in enthalpy (ΔH), changes in entropy (ΔS), and temperature (T):

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

Reactions are favorable when $\Delta G < 0$. Thermodynamically favorable reactions are also called spontaneous reactions. At standard state, Gibbs free energy is given the symbol $\Delta G°$; this is most often the form seen on the AP exam. From the equation above, you should be able to predict whether a reaction is favored given values for enthalpy, entropy, and temperature.

Gibbs free energy of formation (ΔG°_{f}) is the change in free energy needed to convert 1 mole of a substance from its reactants at standard state. ΔG°_{f} is defined by the Gibbs free energy equation, but is generally given in tables as the numbers are standard. Given energy of formation, the **Gibbs free energy of reaction** ($\Delta G^{\circ}_{reaction}$) of a substance is calculated as the difference between the free energy of the substance and its reactants. This describes the amount of heat energy available to do work in a reaction.

$$\Delta G^{\circ}_{\text{reaction}} = \Sigma \Delta G_f{}^{\circ}{}_{\text{products}} - \Sigma \Delta G_f{}^{\circ}{}_{\text{reactants}}$$

In this equation, the sign of $\Delta G^{\circ}_{\text{reaction}}$ tells us which direction the reaction must proceed to reach equilibrium ($\Delta G^{\circ} = 0$), and the size of $\Delta G^{\circ}_{\text{reaction}}$ tells us how far the reaction is from equilibrium.

Note that the overall favorability of the reaction depends on the sum of the free energy of products being greater than the sum of the free energy of reactants. This means that a thermodynamically unfavorable reaction can be made favorable by coupling it with other reactions that are more favorable. For instance, this can occur when the individual reactions share common intermediates. Another way to make a reaction more thermodynamically favorable is to increase energy through an external source, such as electrical energy or a sunlight.

Thermodynamic and Kinetic Control

It is possible for a reaction to be thermodynamically favorable but either occur very slowly or not at all. These reactions are under **kinetic control**. The most common reason for kinetic control of a reaction is that the activation energy is too high for the thermodynamically favorable products to form. Generally, increasing the temperature of a reaction will overcome the activation barrier and form the more thermodynamically favorable product. In this case, the system is under **thermodynamic control**.

Free Energy and Equilibrium

Both equilibrium constant and Gibbs free energy can be used to determine whether a reaction is thermodynamically favored. Remember that this is the case when $\Delta G < 0$ or when $Q < K$. Similarly, the systems are considered at equilibrium when $\Delta G = 0$ or $Q = K$. Thus, it is reasonable that the free energy and equilibrium constant are related (where R is the universal gas constant):

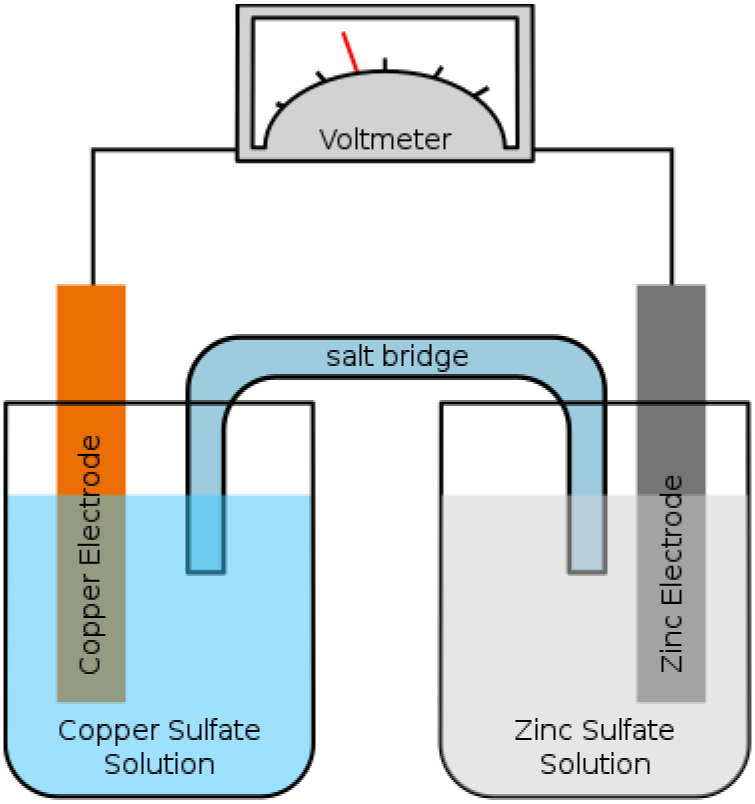
$$K = e^{-\Delta G^{\circ}/RT}$$
$$\Delta G^{\circ} = -RT\ln K$$

You can estimate these constants in relation to each other by considering the above equations. When ΔG is close to zero, you can predict that K will be near 1.

Galvanic (voltaic) and Electrolyte Cells

There are two types of electrochemical cells: galvanic and electrolytic. In both cases, remember that oxidation occurs at the **anode** and reduction occurs at the **cathode**. The anodes and cathodes in both cases are electrodes made of metal. A salt bridge is usually present, which acts as a source of ions that balance building charges.

Galvanic cells, also called voltaic cells, derive energy from thermodynamically favored redox reactions. Galvanic cells are usually made of two half cells connected by a salt bridge. In the example in the following figure, the two half cells are composed of zinc (anode) and copper (cathode) connected by a wire and a salt bridge. When connected, energy flows through the wire from anode to cathode. Energy is harnessed to power devices through the wire connecting the anode and cathode.



Electrolytic cells use a power source to force non-spontaneous reactions to occur, converting electrical energy into chemical energy. In electrolytic cells, electrodes are placed to a liquid containing electrolytes. A battery acts as an electron supply to the negative cathode, which reduces the electrolytes. A positive anode oxidizes and passes the electrons through the circuit.

Cell Potential and Free Energy

A cell's **potential voltage (E_{cell})** is determined by the tendency for the half-reactions to occur spontaneously. To calculate the **voltage of a cell,** break the equation up into half reactions and then add the reduction potential of the oxidation and reduction reactions based on standard reduction potentials (remember that oxidation should be negative). In calculating cell voltage, the coefficients of ions in the reaction are not taken into account. For non-standard conditions, the **Nernst equation** can be used to calculate cell voltage:

$$\mathrm{E_{cell} = E°_{cell} - \frac{RT}{nf}\ln Q}$$

$$\mathrm{R = Ideal\ gas\ constant\ (8.31\ J\ mol^{-1}K^{-1})}$$
$$\mathrm{T = temperature\ (K)}$$
$$\mathrm{n = electrons\ transferred\ (mol)}$$
$$\mathrm{F = Faraday's\ constant\ (96{,}486\frac{C}{mol})}$$
$$\mathrm{Q = reduction\ half\ reaction\ quotient}$$

The Nernst equation, which describes the free energy of an electrochemical cell, is also related to free energy equations given the equation:

$$\Delta G° = -nFE°_{\mathrm{total}} = -RT\ln K$$

If a reaction is thermodynamically favored, the cell will have a positive cell voltage (E°). If the reaction is thermodynamically unfavored, the cell will have a negative cell voltage and require external potential for the reaction to occur.

Under non-standard conditions, cell potential varies depending on concentrations of cell components. The cell potential in this case is the driving force for equilibrium. The farther the reaction is from equilibrium, the greater the cell potential.

The relationship between charge, current, and time is expressed in the equation:

$$\mathrm{Q = It}$$

$$\mathrm{Q = charge\ (C)}$$
$$\mathrm{I = current\ (A)}$$
$$\mathrm{t = time\ (s)}$$

Given this relationship and Faraday's law (1 mol electrons = 96,486 C), quantitative measures can also be calculated for electrolytic cells.

Outside Reading

- For further reading on entropy and the second law of thermodynamics, see:
    - https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Thermodynamics/The_Four_Laws_of_Thermodynamics/Second_Law_of_Thermodynamics

- For further reading on electrolytic cells, see:
    - https://courses.lumenlearning.com/boundless-chemistry/chapter/electrochemical-cells/

Sample Applications of Thermodynamics Questions

Which of the following must be true for a reaction that is thermodynamically favored at both low and high temperatures?

A. ΔH is negative and ΔS is negative.

B. ΔH is negative and ΔS is positive.

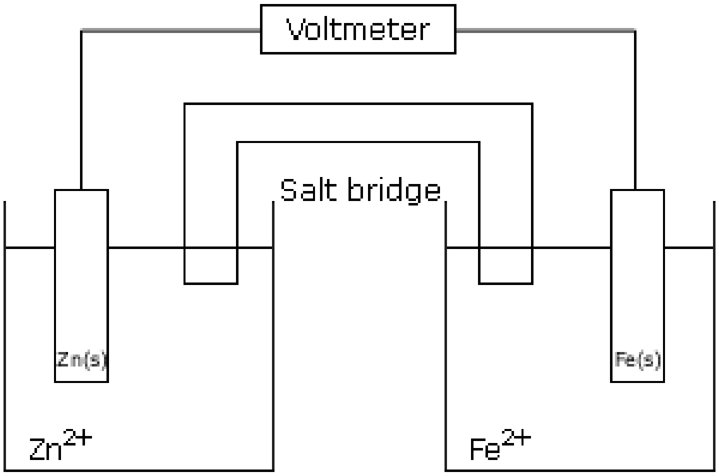
C. ΔH is positive and ΔS is negative.

D. ΔH is zero and ΔS is zero

Explanation:

The correct answer is B. It is not necessary to know the reaction or the values of ΔH and ΔS to answer this question. For a reaction to be spontaneous, ΔG must be negative, which is determined from the equation $\Delta G = \Delta H - T\Delta S$. Therefore, if ΔS is positive, then $-T\Delta S$ will be negative for all temperatures (remember that T is in Kelvin, which is always a positive value). If ΔH is negative and ΔS is positive, then ΔG will be negative for all temperatures and thus spontaneous.

Use the following image to answer the two questions that follow.



In the voltaic cell, which of the following is considered the anode? Assume the standard reduction half-cell potential for iron is −0.44 V and the standard reduction half-cell potential for zinc is −0.76 V.

A. iron metal strip

B. zinc metal strip

C. Fe^{2+} solution

D. Zn^{2+} solution

Explanation:

The correct answer is B. You must determine several things before answering this question. First, you must compare the reduction potentials for the half reactions. $Fe^{2+} + 2e^{-} \rightarrow Fe_{(s)}$ has a reduction potential $E^0 = -0.44$ V and $Zn^{2+} + 2e^{-} \rightarrow Zn_{(s)}$ has a reduction potential $E^0 = -0.76$ V. The half reaction with the more positive E^0 has a greater tendency to reduce, and thus the other half reaction will oxidize. Therefore, the iron (Fe) side will reduce (making it the cathode, choice A), accepting electrons and creating a positively charged cathode. The zinc side (Zn) will oxidize, giving up electrons and creating a negatively charged anode.

In the previous diagram, what would happen to the voltage if 100 ml of 2.0 M $Zn(NO_3)_2$ are added to the beaker on the left?

A. The voltage decreases.

B. The voltage increases.

C. The voltage does not change.

D. The voltage becomes zero.

Explanation:

The correct answer is A. The reaction is $Zn_{(s)} + Fe^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Fe_{(s)}$. $Zn(NO_3)_2$ added to the left beaker increases the Zn^{2+} concentration on the left side and “pushes” the reaction towards the left; this implies a lower voltage.