Chemistry Practice



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Atomic Theory Practice Items

- 1. The weighted average mass of the atoms of the stable isotopes of an element as they occur in nature is called the
 - A. atomic mass
 - **B.** atomic weight
 - C. atomic number
 - **D.** relative isotopic frequency
- 2. Photon energy
 - **A.** is directly proportional to its wavelength.
 - **B.** is inversely proportional to its frequency.
 - C. is directly proportional to its frequency.
 - **D.** equals the wave number.
- **3.** Carbon monoxide has carbon and oxygen in the simple mass ratio 3:4, while carbon dioxide has the ratio 3:8. Similarly, water has oxygen and hydrogen in the simple mass ratio 8:1, while hydrogen peroxide has the ratio of 16:1. These examples illustrate which of the following?
 - **A.** conservation of matter and energy
 - **B.** the Bohr frequency rule
 - **C.** the law of partial pressures
 - **D.** the law of multiple proportions
- 4. A cathode ray
 - **A.** consist of a stream of positively charged particles.
 - **B.** will not be affected in passing through an orthogonal electric field.
 - C. is composed of electrons.
 - **D.** possesses no mass.

- **5.** Analysis of the emission spectrum of hydrogen led Bohr to conclude that
 - **A.** the hydrogen atom consists of an electron and a proton.
 - **B.** electron energy states are quantized.
 - C. light comes in discreet packages of energy called quanta.
 - **D.** one cannot determine the exact position of an electron concurrently with its exact momentum.
- 6. In the Bohr theory of the atom the energy of the *n*-th level for any atom is given by the following equation

where *Z* is the atom's atomic number. Which of the following would be predicted by the Bohr model of the hydrogen atom?

- **A.** The ionization energy of hydrogen is equal to 13.6 eV.
- **B.** The electron affinity of hydrogen is equal to 0.75 eV.
- **C.** The lowest possible energy state of a hydrogen atom is zero.
- **D.** A longer wavelength photon is absorbed in elevating an electron from the ground state to the 2nd energy level than from the 2nd to the 3rd.
- 7. In the Schroedinger model, which of the following describes the shape of the orbital inhabited by an electron?
 - A. principle quantum number, *n*
 - **B.** magnetic quantum number, m_1
 - C. angular momentum quantum number, l
 - **D.** spin quantum number, m_s

Questions 8 and 9 are based on the following energy level diagram for the hydrogen atom.



- 8. Of the labeled electronic transitions shown in the figure, photons of the shortest wavelength are being emitted by the atom by the transition labeled:
 - **A.** A
 - **B.** B
 - **C.** C
 - **D.** D
- 9. The arrow representing ionization energy is:
 - **A.** A
 - **B.** B
 - **C.** C
 - **D.** D
- **10.** How many p-orbitals are occupied in a ground state Ne atom?
 - **A.** 1
 - **B.** 2
 - **C.** 3
 - **D.** 6

11. Which of the following is the proper ground state orbital diagram for neutral carbon?

A.
$$1s$$

 $(\uparrow \downarrow)$ $2s$
 $(\uparrow \downarrow)$ $2p$
 $(\uparrow \downarrow)$ B. $1s$
 $(\uparrow \downarrow)$ $2s$
 $(\uparrow \downarrow)$ $2p$
 $(\uparrow \downarrow)$ C. $1s$
 $(\uparrow \downarrow)$ $2s$
 $(\uparrow \downarrow)$ $2p$
 $(\uparrow \downarrow)$ D. $1s$
 $(\uparrow \downarrow)$ $2s$
 $(\uparrow \downarrow)$ $2p$
 $(\uparrow \downarrow)$

- **12.** An electron exists in a *p* orbital, therefore
 - A. the principle quantum number is at least 1.
 - **B.** the angular momentum quantum number must be 2.
 - **C.** the spin number must be either -1 or 1.
 - **D.** the magnetic quantum number could be either -1, 0, or 1.
- 13. Which of the following electronic configurations is the ground state configuration for ruthenium (Z = 44)?
 - **A.** [Kr] $5s^2 4d^6$
 - **B.** [Kr] $4s^2 4d^6$
 - **C.** [Kr] 4d⁸
 - **D.** [Kr] $5s^1 4d^7$

The following passage pertains to questions 14-18.

In 1913 Henry Moseley found an empirical relationship between the strongest X-ray line emitted by metals under electron bombardment and their atomic number Z.

In contrast to the UV and visible light spectrometers employed on similar work with hydrogen by researchers such as Ångström and Lyman, Moseley required an X-ray spectrometer for his work with metals. Inside an evacuated glass-bulb electron tube, electrons were fired at a pure metallic substance, causing the ionization of electrons from the inner electron shells of the element. The rebound of electrons into these holes in the inner shells caused the emission of X-ray photons. These exited the tube in a semi-beam, through an opening in the external X-ray shielding. The X-ray photons were next diffracted by a standardized salt crystal, with angular results recorded by X-ray film oriented a fixed distance from the vacuum tube. Analysis of the diffraction pattern allowed the wavelength of the emitted X-rays to be calculated.

The energy lost by an electron dropping from the second shell to the first is described by Moseley's law for K-alpha lines:

$$E = hf = E_{\rm i} - E_{\rm f} = R_{\rm E}(Z - 1)^2 \left(\frac{1}{1^2} - \frac{1}{2^2}\right)$$

Z is atomic number and $R_{\rm E}$ is the Rydberg constant, equal to $2.180\times10^{-18}\,J.$

It was assumed that this X-ray line came from a transition between energy levels with quantum numbers 1 and 2. Moseley's empiric formula was found to be derivable from earlier formulas put forth by Rydberg and Bohr, but the atomic number Z when used in the formula for atoms heavier than hydrogen was diminished by 1 to (Z-1).

At the time it was thought that the innermost "K" shell of electrons should have at least four

electrons, so Moseley published his results without a theoretical explanation for the reduction in atomic number by 1. Later, after the inner shell was demonstrated to contain only 2 electrons, it was realized that the effect was caused by charge screening. In the experiment, one of the innermost electrons in the atom is knocked out, leaving a vacancy in the lowest Bohr orbit, which contains a single remaining electron. Therefore, the n=2 electrons aren't pulled inward by the full nuclear charge of +Z but an effective charge of Z–1.

Moseley's law not only established the objective meaning of atomic number, but, as Bohr noted, it established the validity of the nuclear model of the atom with place on the periodic table determined by whole units of nuclear charge.

- **14.** Which of the following statements is true regarding Moseley's model of X-ray production by metal atoms under electron bombardment?
 - **A.** The model could account for the emission spectrum of hydrogen.
 - **B.** The model was based on the wave properties of the electron.
 - **C.** The model was successful in explaining the systematic variation of X-ray emission spectra with atomic number.
 - **D.** The model provided the first coherent description of the photoelectric effect.
- **15.** Following the ejection by X-rays of electrons from the inner shells of metal atoms, the rebound of electrons into these holes
 - A. causes ionization of the metal atom.
 - **B.** corresponds to a decrease in the energy of the metal atom.
 - **C.** occurs across a distance equal to the wavelength of the emitted X-ray.
 - **D.** occurs with absorption of an X-ray.

- **16.** Which of the following can be deduced from the information presented in the passage?
 - **A.** X-rays are required to ionize larger metal atoms.
 - **B.** An electron transition from the K shell to the L shell may cause a metal atom to release an X-ray photon.
 - **C.** An X-ray photon is produced by ionization when a high energy electron collides with a ground state metal electron.
 - **D.** The transition energy for an electron from quantum number 2 to 1 is greater with large atoms than with hydrogen.
- 17. Why is the appropriate charge for the nucleus acting on a rebounding electron from the n=2 shell equal to (Z 1) in the Moseley formula?
 - **A.** An electron in the lowest Bohr orbit screens the nuclear charge.
 - **B.** The ejected electron leaves a vacancy in the lowest Bohr orbit.
 - **C.** It was thought that the innermost shell should have at least four electrons.
 - **D.** The emission of a positron decreases the nuclear charge.
- **18.** Which of the following data might have been collected during the empirical derivation of Moseley's Law?
 - **A.** a graph showing a geometric increase in emission wavelength with atomic number
 - **B.** a graph showing logarithmic increase of emission frequency with atomic number
 - **C.** a graph showing an exponential increase in emission frequency with atomic number.
 - **D.** a linear plot of the square root of X-ray frequency against atomic number

Atomic Theory

Answers and Explanations

1. B

The atomic weight of an element is the weighted mean of the relative atomic masses of all isotopes of that element weighted to reflect each isotope's abundance on Earth. For example, the atomic weight of the element chlorine is 35.45u. This is determined by averaging the atomic masses and relative abundances of its two main naturally occurring isotopes, which have atomic masses of 34.97u (76%) and 36.97u (24%).

2. C

Photon energy equals the product of Planck's constant ($h = 6.63 \times 10^{-34} \text{ J} \cdot \text{s}$) and the frequency of the light.

E = hf

3. D

The law of multiple proportions, sometimes called Dalton's Law, was a key proof of atomic theory. The law states that if two elements form more than one compound between them, then the ratios of the masses of the second element combined with a fixed mass of the first element will always be ratios of small whole numbers.

4. C

A cathode ray is a stream of electrons produced in a particular type of vacuum tube apparatus, ie. an evacuated glass tube equipped with two electrodes across which a powerful voltage is applied.



Cathode ray tubes played an important role in the history of atomic theory. In 1897 J. J. Thomson demonstrated that cathode rays were made of particles approximately 1800 times lighter than hydrogen atoms. In other words, the first subatomic particle to be discovered, the electron, was characterized using a cathode ray apparatus. Thomson showed the particles of a cathode ray were identical with particles given off by photoelectric and radioactive materials. It was quickly recognized that electrons are the particles within an atom in possession of negative electric charge.

5. B

When hydrogen atoms are excited by heat or electricity they emit light. However, instead of the continuous spectrum predicted by the classical model of an atom, one observes a line spectrum, with only particular wavelengths represented. Below is a portion of the line spectrum in the visible region for hydrogen.



Bohr reasoned that the line spectrum was evidence that the hydrogen atom electron could exist only in certain discrete, quantized energy states. The energy of the line spectrum photons is related to the energy differences between these states through the Bohr frequency rule: $hf = E_f - E_i$

6. A

In the classical model of the energy of a system of two oppositely charged point charges, the sum of the potential and kinetic energy is less than zero when the system is bound. The distance to zero equals the energy required to pull apart the oppositely charged particles. The Bohr model also presents the hydrogen atom as a system where the sum of potential and kinetic energy is a number less than zero. The energy states are a series of negative numbers. For hydrogen's single electron, the energy of the ground state equals -13.6 eV.

Ionization energy is the minimum energy required to remove an electron from a neutral gaseous atom in the ground state. For hydrogen, this means elevating the electron from -13.6 eV to zero, which is the threshold for the electron to escape from the atom. In other words, the ionization energy of hydrogen is 13.6 eV.

7. C

The orbital angular momentum quantum number, l, also known as the azimuthal quantum number, is the quantum number that determines the shape of the orbital. If l = 0, the electron is in an *s* subshell. If l = 1, the electron is in an *p* subshell, and if l = 2, the electron is in an *d* subshell.

8. B

In the Bohr hydrogen atom, the electron exists in one of a series of allowed orbits, called stationary states. The atom emits a photon when the electron transitions from one stationary orbit to another. The emitted photon energy equals the energy difference of the stationary states, the Bohr frequency rule.

$$hf = E_{f} - E_{i}$$

Of the labeled transitions, only the transitions labeled B and D depict an electronic transition in which the electron is falling inward towards the nucleus, decreasing in energy, so those are the only two of the four which correspond to emission of energy. A and C correspond to absorption of energy by the atom.

The vertical scale on the energy diagram is straightforward. The transition from n = 4 to n = 3, labeled B, will be the transition involving the greatest change in energy that produces the shortest wavelength photon. The higher the frequency the shorter the wavelength.

$$E = hf$$
 $E = \frac{hc}{\lambda}$

9. A

Ionization energy is the minimum energy required to remove an electron from a neutral gaseous atom in the ground state. For hydrogen with only a single electron, ionization energy corresponds to the transition of this electron from its position at n = 1 to ∞ .

10. C

With a ground state electron configuration of $1s^22s^22p^6$, the electron orbital diagram of neon shows the three *p* orbitals completely occupied.

$$\begin{array}{cccc} 1s & 2s & 2p \\ (\uparrow \downarrow) & (\uparrow \downarrow) & (\uparrow \downarrow) & (\uparrow \downarrow) & (\uparrow \downarrow) \end{array}$$

11. C

By Aufbau principle, the electrons fill the lower energy 1s and 2s orbitals first. The remaining two electrons then, by Hund's rule, go into the 2p orbitals singly with parallel spin.

12. D

For an electron in a p orbital, regarding the first three incorrect choices, the principle quantum number must be at least 2 (not at least 1). The angular momentum quantum number must be 1 (not 2). The spin number must be either -1/2 or 1/2 (not -1 or 1).

The correct choice is '**D**'. When the angular momentum quantum number is equal to 1, and the electron is within a p subshell, the magnetic quantum number could be either -1, 0, or 1. In other words, there are three orbitals within a p subshell which the electron might occupy.

13. D

The purpose of this question is to broaden the perspective toward the build-up order for heavier elements. It's okay to miss this question! Textbooks teach the "Madelung order":

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < etc.$$

This order explains the electron configurations of the first three periods of the periodic system and of the first two elements of the forth period, K and Ca. For Ca, for example, 4s < 3d, but for Sc and subsequent 3d < 4s. This is important to remember. The outermost *s* electrons are always the first to be removed in the process of forming transition metal cations.

In the case of ruthenium, because the 4d shell is rather compact, in contrast to the diffuse 5s orbital, the electron repulsion in the d shell increases with increasing d occupation. Eventually, it becomes energetically favorable to shift one of the electrons from the 4d shell into the slightly higher energy 5s orbital.

The basic lesson of this question is not to assume a simple Madelung build-up order for larger atoms.

14. C

Moseley's model relates the photon energy of emitted X-rays to the transition energy of inner shell electrons, which itself depends on nuclear charge, ie. atomic number.

15. B

When an electron falls from the second shell to the first, negative charge is moving closer to positive charge. This represents a decrease in electrostatic potential energy. The energy lost equals the energy of the emitted photon.

16. D

There are many direct and indirect references to the greater energy involved for inner shell transitions of larger atoms compared to hydrogen. The passage describes how Moseley required an X-ray spectrometer to analyze the emission spectra, unlike the UV and visible light spectrometers employed on similar work with hydrogen by researchers such as Ångström and Lyman. X-rays are higher energy photons than UV and visible light. Additionally, Moseley's law for K-alpha lines shows increased energy with increased atomic number, and the passage later refers to the dependence of the transition energy on nuclear charge.

17. A

From the perspective of the rebounding electron, falling from the L shell to the K shell, it is falling towards a nucleus shielded by the single remaining inner shell electron. This is the other electron in the first shell which had not been ejected by earlier the bombardment of the atom.

18. D

Moseley's law for K-alpha lines describes the linear dependence of the square root of emission frequency on atomic number. For simplification, the illustration below bundles all of the constants into 'm'.

$$E = hf = E_{i} - E_{f} = R_{E}(Z - 1)^{2} \left(\frac{1}{1^{2}} - \frac{1}{2^{2}}\right)$$
$$hf = R_{E}(Z - 1)^{2} \left(\frac{1}{1^{2}} - \frac{1}{2^{2}}\right)$$
$$Z = m\sqrt{f} + 1$$

Periodic Properties Practice Items

- **1.** Upon what basis did Mendeleev construct his periodic table?
 - A. the electron configuration of atoms as determined by emission spectra
 - **B.** the atomic radii of the elements as determined by α particle collision data
 - **C.** the variation of chemical properties with atomic weight
 - D. the periodic nature of electronegativity
- 2. Why do non-metals have high ionization energies?
 - A. They are very large atoms and thus have a stronger hold on their electrons.
 - **B.** They are on the right side of the periodic table.
 - **C.** High effective nuclear charge provides a stronger hold on outer shell electrons.
 - **D.** Their outer shell electrons are shielded from the nuclear charge.
- 3. Which has higher first ionization energy?
 - **A.** lithium
 - **B.** aluminum
 - C. boron
 - **D.** carbon

- 4. Which of the following statements is **true**?
 - **A.** Fluorine is less electronegative than chlorine.
 - **B.** Potassium has greater ionization energy than sodium.
 - **C.** Nitrogen has a greater electron affinity than carbon.
 - **D.** Carbon has a greater atomic radius than oxygen.
- 5. Which of the following statements is consistent with the table below?
 - **A.** The more electropositive the central atom of an oxide the more basic the oxide.
 - **B.** The larger the central atom of the oxide the more acidic the oxide.
 - **C.** The oxides of non-metals are acidic.
 - **D.** Nonmetal oxides react with acids to produce salts

Acidity or basicity of oxides of s- and p- block elements when dissolved in water						
Li	Be		С		0	
Na	Mg	Al				Cl
K	Ca	Ga	Ge	As	Se	Br
Rb	Sr	In	Sn	Sb		
Cs	Ba	Tl	Pb	Bi	Ро	At
Basic Oxides		Amphoteric Oxides		Acidic Oxides		

- **6.** Which of the following elements has an electronegativity value of 1.0 on the Pauling scale?
 - A. calcium
 - **B.** carbon
 - C. hydrogen
 - D. oxygen

- 7. All of the following can be measured **except**
 - **A.** the ionization energy of krypton.
 - **B.** the atomic radius of hydrogen.
 - C. the Pauling electronegativity of helium.
 - **D.** the electron affinity of lithium.
- 8. The graph below shows the variation across the 2nd period of the periodic table of this property
 - A. ionization energy
 - **B.** electron affinity
 - **C.** atomic radius
 - **D.** electronegativity



- 9. Which ion has the smallest radius?
 - A. Be^+
 - **B.** Li⁺
 - **C.** F⁻
 - **D.** O^{2-}
- **10.** For which group is the difference between the first and second ionization energy the greatest?
 - A. alkali metals
 - **B.** alkaline earth metals
 - C. halogens
 - **D.** noble gases

- 11. The following elements appear prominently in organic chemistry – carbon, hydrogen, oxygen, nitrogen, and sulfur. Which two are closest to each other in Pauling electronegativity?
 - A. carbon and sulfur
 - **B.** oxygen and nitrogen
 - C. carbon and hydrogen
 - **D.** sulfur and nitrogen
- **12.** Which of the following elements possesses an electron affinity that is actually endothermic?
 - A. carbon
 - B. nitrogen
 - C. oxygen
 - D. fluorine
- **13.** For which of these salts does the bond between the anion and cation possess the greatest covalent character?
 - A. CaBr₂
 - **B.** AgCl
 - C. KI
 - D. NaOH
- **14.** In comparing the standard state forms of various elements, which of the following properties is more positive the greater the Pauling electronegativity of the element?
 - A. standard reduction potential
 - **B.** electron affinity
 - C. brittleness
 - **D.** electric conductivity

The following passage pertains to questions 15 - 17.

Linus Pauling first proposed the concept of electronegativity in 1932. The concept explained the additional stabilization of a heteronuclear bond in terms of the contribution of ionic forms to an underlying covalent bond. The difference in electronegativity between atoms A and B is given by:

$$\chi_{\rm A} - \chi_{\rm B} = (eV)^{-1/2} \sqrt{E_{\rm d}({\rm AB}) - [E_{\rm d}({\rm AA}) + E_{\rm d}({\rm BB})]/2}$$

where the dissociation energies, $E_{\rm d}$, of the A–B, A–A and B–B bonds are expressed in electron volts. Hence, for hydrogen and bromine, the dissociation energies H–Br, 3.79 eV; H–H, 4.52 eV; Br–Br 2.00 eV entail a difference in Pauling electronegativity of 0.73 between hydrogen and bromine.

One consequence of the Pauling electronegativity scale is that it provides a semi-empirical formula to determine dissociation energies. This energy estimate can be only used for single, not multiple bonds.

$$E_{d}(AB) = [E_{d}(AA) + E_{d}(BB)]/2 + (\chi_{A} - \chi_{B})^{2}eV$$

As only differences in electronegativity are defined, it is necessary to choose an arbitrary reference point in order to construct a scale. Because it forms covalent bonds with a large variety of elements, hydrogen was chosen as the reference, fixed at 2.1 (later revised to 2.2).

- **15.** A heteronuclear covalent bond in which there is a strong contribution of ionic forms to the underlying covalent bond is a
 - A. π bond
 - **B.** σ bond
 - **C.** polar covalent bond
 - **D.** coordinate covalent bond

- **16.** Which statement below follows from the method of determining bond dissociation energies described in the passage?
 - **A.** Polar bonds tend to be stronger than nonpolar bonds.
 - **B.** Bond formation between two atoms with high electronegativity tends to be very exothermic.
 - **C.** The electronegativity difference between bonded atoms determines whether the bond is a single or double bond.
 - **D.** Bond dissociation energy increases with ionization energy.
- **17.** According to the theory underlying the electronegativity scale, which of the following is closest to the contribution made by the polar character of the bond to the bond dissociation energy of H–Br?

A.	0.53 eV
B.	0.63 eV
C.	0.73 eV
D.	2.52 eV

Periodic Properties

Answers and Explanations

1. C

The fundamental observation was that the elements, if arranged according to their atomic weight, exhibit a periodicity of properties.

2. C

The nonmetal elements occupy the upper righthand corner of the period table. Across a period from left to right, effective nuclear charge increases. With each step to the right the nucleus gains a proton, but the shielding of the nucleus by inner shell electrons remains constant. The greater effective nuclear charge pulls the electron cloud closer to the nucleus, strengthening the nuclear attraction to the outer-most electron so the general trend with movement towards the right is that removing an electron will require greater energy.

3. D

Moving left to right within a period, the first ionization energy generally increases. Moving downward within a group, ionization energy decreases.

4. D

Moving left to right within a period, atomic radius *decreases*. Even though the atoms are becoming more massive, the greater effective nuclear charge pulls the electron cloud closer to the nucleus.

Note that choice 'C' is untrue. Electron affinity of carbon is greater than nitrogen even though the general trend is for electron affinity to increase left to right. The electron affinity of nitrogen is actually slightly endothermic, because nitrogen has a half filled p orbital. Three single electrons with parallel spin in the three p orbitals is particularly stable. Nitrogen is an important exception both in electron affinity, which is much lower than you would expect and in ionization energy which is higher than you would expect.

5. C

Oxides are chemical compounds with one or more oxygen atoms combined with another element. Based on their acid-base characteristics oxides are classified as acidic, basic, amphoteric or neutral. An oxide that combines with water to give an acid is termed as an acidic oxide. As the table accompanying the question shows, the oxides of nonmetals are acidic.

6. A

Electronegativity on the Pauling scale runs from 0.79 (cesium) to 3.98 (fluorine). A good rule of thumb for alkali and alkaline earth metals is that their electronegativity is close to 1. For example, sodium is 0.93. Magnesium is 1.3. Calcium is 1.0.

7. C

Pauling electronegativity describes the tendency of an atom to pull a shared pair of electrons towards itself. Helium is not listed because it does not form covalent bonds.

8. C

Moving left to right within a period, atomic radius is the only trend that *decreases*. Even though the atoms are becoming more massive, the greater effective nuclear charge pulls the electron cloud closer to the nucleus.

9. B

Lithium ion has lost its only L shell electron, so it now has an atomic radius nearer to helium than a 2nd period element. All of the other choices possess outer shell electrons in the L shell.

10. A

Alkali metals have one outer shell electron. The first ionization energy is low because after losing one electron the cationic species will achieve noble gas configuration. However, if we try to remove a second electron that will require a very large amount of energy because it will disturb the noble gas configuration. That's why first ionization energy of alkali metals is low and second ionisation energy is high.

11. A

Memorize the number values of the electronegativities of the elements that play a prominent role in organic chemistry. Along with valence, electronegativity is the window into the 'personality' of an element. Sulfur becomes increasingly important in biochemistry. The electronegativity of sulfur is 2.58, just a hair higher than the electronegativity of carbon at 2.55. While thet carbon-sulfur bonds are *nonpolar*, sulfur oxidizes carbon. It is more electronegative, so sulfur gets to claim the electrons carbon brings to bonding with sulfur.

12. B

Nitrogen is an exception to the general trend of electron affinity increasing from left to right on the periodic table. Nitrogen has a half-filled 2p subshell, so that there is one electron in each orbital. This creates an unusually stable atom because of half-shell stability. The electron affinity of nitrogen is actually slightly endothermic. The additional electron disturbs the harmony of three electrons with parallel spin in the 2p subshell.

13. B

For all of the salts among the answer choices except AgCl, the cation species is the ion of an alkali metal or an alkaline earth metal. Alkali metals and alkaline earth metals have an electronegativity of approximately 1, so paired with oxygen or a halogen, the electronegativity difference reflects an ionic bond. Silver, on the other hand, is a much more electronegative transition metal. Its electronegativity on the Pauling scale is 1.93. Its bond to chlorine in AgCl has significant covalent character. Greater covalent character is one of the reasons a salt may be insoluble or sparingly soluble.

14. A

In the twentieth century, the methods of problem solving in oxidation-reduction grew out of the fun-

damental discoveries behind Pauling's electronegativity scale. When a very electronegative element forms a covalent bond, it pulls the electrons in the bond in towards its powerful nucleus. This makes the bond stronger. In electrochemistry, we conceptualize the electron falling towards a positive potential. A powerful oxidizing agent is being reduced.

15. C

Linus Pauling proposed an empirical relationship which relates the percent ionic character in a bond to the electronegativity difference. Bonds for which the electronegativity difference is greater than 1.7 are said to have greater than 50% ionic character. Bonds with significant ionic character, though less than 1.7 electronegativity difference, are polar covalent bonds. In polar covalent bonding the pair of electrons is unequally shared between two atoms.

16. A

The formula below presents a picture in which the greater the electronegativity difference between elements A and B, the greater the additional bond dissociation energy due to the partial ionic character of the bond, ie. the polar character.

$$E_{d}(AB) = [E_{d}(AA) + E_{d}(BB)]/2 + (\chi_{A} - \chi_{B})^{2}eV$$

The greater the bond dissociation energy, the more energy is required to break the bond. Polar covalent bonds tend to be stronger.

17. A

$$E_{d}(AB) = [E_{d}(AA) + E_{d}(BB)]/2 + (\chi_{A} - \chi_{B})^{2}eV$$

In the formula above, the contribution of the polar character of the bond to the bond dissociation is represented by the term: $(\chi_A - \chi_B)^2 eV$. As described in the passage, the electronegativity difference of hydrogen and bromine is 0.73. Therefore the contribution of the polar character is $(0.73)^2$ cV = 0.53 eV.

Chemical Bonding Practice Items

- 1. Covalent bonds
 - A. are a kind of Van der Waals force.
 - **B.** involve the sharing of electrons between atoms.
 - **C.** consist of the electrostatic attraction between ions.
 - **D.** concentrate the greatest electron density outside the internuclear axis.
- **2.** Ionic bonding occurs in the following pair of elements:
 - A. C and Cl
 - **B.** Cu and I
 - C. Mg and Cl
 - **D.** C and S
- **3.** Isoelectric species have the same electron configuration. Which of the following does not belong in the same group of isolectric species with the others?
 - A. O^{2–}
 - **B.** F[−]
 - C. Na⁺
 - **D.** Ar
- 4. Sulfur can form a transargononic compound with fluorine, SF_6 , in which the atomic orbitals of sulfur hybridize to form six sp^3d^2 orbitals. What is the shape of the molecule?
 - A. trigonal bipyramidal
 - **B.** tetrahedral
 - C. octahedral
 - D. planar

- 5. Two Lewis structures may be drawn for SO_2 that obey the octet rule. Bond lengths and bond energies in SO_2
 - **A.** correspond to a sulfur-oxygen single bond and a sulfur-oxygen double bond.
 - **B.** lie between those expected for sulfur-oxygen double and triple bonds.
 - **C.** demonstrate periodic fluctuation between single and double bonds.
 - **D.** are identical for the two sulfur-oxygen bonds.
- 6. The H–O–H bond angle in water equals
 - **A.** 104.5°
 - **B.** 109.5°
 - **C.** 120°
 - **D.** 180°
- 7. Which of the following molecules is linear?
 - **A.** H₂O
 - **B.** NO_2
 - C. SO_2
 - **D.** CO_2
- 8. Bonding in ozone (O_3) can be expressed as a resonance hybrid.



The angle formed by the three oxygens in ozone is nearest to

- **A.** 109°
- **B.** 117°
- **C.** 120°
- **D.** 180°

Chemical Bonding

- **9.** Which of the following reactions at standard temperature and 0.01 atm between atomic species would be most exothermic?
 - **A.** $H(g) + F(g) \longrightarrow HF(g)$
 - **B.** $H(g) + Cl(g) \longrightarrow HCl(g)$
 - **C.** $H(g) + Br(g) \longrightarrow HBr(g)$
 - **D.** $H(g) + I(g) \longrightarrow HI(g)$

The energy diagram for the formation of H_2 below pertains to questions 10 and 11.



- **10.** From the diagram we can conclude that
 - **A.** at distances less than 0.74Å the repulsion between the electrons increases sharply.
 - **B.** breaking the bonds of hydrogen molecules releases 432 kJ/mole of energy.
 - **C.** 0.74Å is the H_2 bond distance.
 - **D.** when two hydrogens share a pair of electrons, the spins of the electrons become paired.

- 11. Suppose that instead of H_2 formation the diagram showed formation of N_2 .
 - **A.** The internuclear distance at the curve minimum would be lower.
 - **B.** The depth of the energy well would be greater.
 - C. There would be three minima.
 - **D.** The energy would be greatest for large values of internuclear distance.

- **12.** Determine the kind of hybrid orbitals used by sulfur in SF_4
 - A. sp^2
 - **B.** sp^{3}
 - **C.** sp^3d
 - **D.** $sp^{3}d^{2}$

- **13.** How many carbons in ubiquinone, pictured below, are sp^2 hybridized?
 - **A.** 6
 - **B.** 8
 - **C.** 26
 - **D.** 28



The following molecular orbital electron configurations pertain to questions 14 - 16:



- **14.** Which molecule is shown by its molecular orbital electron configuration to have a bond order of 1?
 - **A.** N₂
 - **B.** O_2^{-}
 - C. F_2
 - **D.** Ne $_2$
- **15.** Which molecule is shown by its molecular orbital electron to be unstable?
 - **A.** N₂
 - **B.** O_2
 - C. F_2
 - **D.** Ne₂
- **16.** Which molecule is shown by its molecular orbital electron configuration to be paramagnetic?
 - **A.** N₂
 - **B.** O₂
 - C. F_2
 - **D.** Ne $_2$

Chemical Bonding

Answers and Explanations

1. B

A covalent bond involves the sharing of electron pairs between atoms leading to a stable balance of attractive and repulsive forces between atoms. In many cases, the sharing of electrons allows each atom to attain the equivalent of a full outer shell, which is a stable electronic configuration.

2. C

As with Mg (electronegativity 1.3) and Cl (electronegativity 3.1), a bond will be ionic (> 50% ionic character) when the electronegativity difference between bonded atoms is 1.7 or greater. Ionic bonding occurs when elements from the far left of the periodic table (alkali and alkaline earth metals) form compounds with the more electronegative nonmetals from the right side of the periodic table.

3. D

 O^{2-} , F^- and Na^+ possess the same configuration as neon, not argon.

4. C

The premise of valence shell electron pair repulsion theory (VSEPR) is that the valence electron pairs surrounding an atom tend to repel each other and adopt an arrangement that minimizes this repulsion. In SF_6 there are six electron pairs in the covalent bonds between sulfur and fluorine. The geometry that results is octahedral.



5. D

Sulfur dioxide has two resonance structures which contribute equally to the overall hybrid structure of the molecule.



6. A

The H–O–H bond angle in water equals 104.5°. There are four regions of electron density around oxygen - the two electron pairs in the covalent bonds plus the two nonbonded pairs, the geometry is based on the tetrahedron, but the angle is not the tetrahedral angle of 109.5° because the nonbonded pair repulsions are stronger.



7. D

With all of its electrons participating in the double bonds to the two oxygens, the carbon of CO_2 has two regions of electron density. A double bond is considered a single region of electron density in VSEPR. This produces a linear geometry. In other words, the O-C-O bond angle is 180°.

$$\ddot{o} = c = \ddot{o}$$

8. B

Molecules with three regions of electron density have a geometry that is trigonal planar, so one might expect the O-O-O bond angle to be 120°. However, lone pairs of electrons are slightly more repulsive than bonding pairs of electrons. Therefore the O-O-O angle is a few degrees less than 120°.

9. A

The energy released when the bond is formed is the bond dissociation energy. The respective bond dissociation energies for the respective hydrogen-halogen bonds is as follows: Bond dissociation energy – kJ mol⁻¹

HF	570
HCl	432
HBr	366
HI	298

As a general rule, bonds with greater electronegativity difference have greater bond dissociation energy. There is not only the decrease in energy as the atoms fall into the well of binding energy associated with a normal chemical bond pulling the nuclei together. There's an additional decrease in energy as the electronegative element pulls the bonding electrons in towards its nucleus.

10. A

Bond length or bond distance is defined as the average distance between nuclei of two bonded atoms in a molecule. In the energy diagram, there is an energy minimum at 0.74 Å. Think of the energy to pull the two atoms apart from this distance due to the attractive force exerted by the electrons within the sigma bonding orbital between them. It would also take energy to push the two atoms any nearer to each other due to the repulsive force of the two nuclei. Due to the thermal energy, the two atoms will be vibrating much like a mass-spring oscillator with the bond distance analogous to the the equilibrium position of the oscillator.

11. B

Because it is a triple bond, the bond dissociation energy of N_2 (945 kJ/mol) is greater than the bond dissociation energy of H_2 . In forming the bond, the nitrogen atoms fall together into a deeper well of electrostatic potential energy.

12. C

Sulfur has six valence electrons. Fluorine has seven. Constructing the Lewis dot structure of SF_4 , after completing the octets of the fluorine atoms in the molecule, sulfur has one pair of electrons remaining.



Along with phosphorus, having access to d subshell orbitals, sulfur is a prominent example of an element that can form an 'expanded octet.' Here, to accommodate five pairs of electrons, sulfur undergoes sp^3d hydridization. This is the only choice available with five orbitals.

13. C

There are 26 sp^2 hybridized carbons depicted – 6 in the benzoquinone ring and 20 in the isoprenoid tail.



14. C

In F_2 there is one more pair of electrons in bonding orbitals than in antibonding orbitals, corresponding to a bond order of 1.

15. D

In the Ne_2 molecular orbital diagram there are equal numbers of electrons in bonding and antibonding orbitals. The bond order is zero. Any covalent bonding interaction would be transitory and unstable.

16. B

The O_2 molecular orbital diagram provides the explanation for why the O_2 molecule is paramagnetic. There are two singlet electrons in antibonding orbitals. With O_2 you have, a triple bond with two additional singlet electrons in antibonding orbitals. The bond order is 2.

Stoichiometry Practice Items

- 1. How many moles of C_2H_6 are present in 600 mg?
 - A. .002 moles
 - **B.** .02 moles
 - **C.** 10 moles
 - **D.** 20 moles
- 2. How many grams of acetylene combine with 500 g Br_2 in a reaction to completion to form $C_2H_2Br_4$?
 - **A.** 10 g
 - **B.** 41 g
 - **C.** 81 g
 - **D.** 250 g
- **3.** Germanium is an element used in semiconductors. How many atoms of germanium are there in 35.5g of germanium?
 - A. 8.0×10^{18}
 - **B.** 1.6×10^{19}
 - **C.** 2.9×10^{23}
 - **D.** 1.2×10^{24}
- **4.** Which is the sum of the coefficients in the following equation when balanced?
 - $HCl + Cr \longrightarrow CrCl_3 + H_2$
 - **A.** 6
 - **B.** 9
 - **C.** 13
 - **D.** 14

5. A compound with empirical formula C_2CIH was analyzed by mass spectrometry. What is the molecular formula of the compound?



6. What is the simplest chemical formula for the following compound, which has this percent composition by weight?

carbon 39% hydrogen 16% nitrogen 45%

- **A.** CH_5N **B.** C_2H_7N **C.** $C_2H_6N_2$ **D.** C_3H_9N
- 7. After hydrated magnesium sulfate was heated for a prolonged period, the remaining salt was found to have lost 51% of its weight. What was the original formula for the hydrate?

A. $MgSO_4-2H_2O$ **B.** $MgSO_4-4H_2O$ **C.** $Mg_2SO_4-8H_2O$ **D.** $MgSO_4-7H_2O$

- 8. A scientist carries out the complete combustion in the air of 44 grams of the compound $C_aH_bO_c$. 36 grams of water vapor and 88 grams of carbon dioxide are produced. What is the empirical formula of the compound?
 - **A.** $C_4 H_8 O_1$
 - **B.** $C_2H_4O_1$
 - **C.** $C_2H_5O_1$ **D.** $C_4H_4O_1$
- **9.** Acetylene is produced in a reaction between calcium carbide and water.

 $CaC_2 + 2H_20 \longrightarrow CaOH_2 + C_2H_2$

How many grams of C_2H_2 (acetylene) would be formed if 18 ml of water is consumed?

- **A.** 13 g**B.** 18 g
- **C.** 26 g
- **D.** 28 g
- The combustion of one mole of an unbranched alkane yields 157 liters of gas at STP. The molecular formula of this compound is
 - $\mathbf{A.} \quad \mathbf{C}_{2}\mathbf{H}_{6}$
 - **B.** C_3H_8
 - **C.** C_4H_{10}
 - **D.** C_5H_{12}

- 11. Seeking to verify the identity of a metal, a laboratory determines that the metal combines with oxygen to form a compound with the formula X_2O_3 . 1.6 grams of oxygen combine with 6.75 grams of the unknown metal X. What is the identity of the metal?
 - A. Fe
 - **B.** Ru
 - C. Os
 - D. Pb
- **12.** How many grams of methanol are formed when 14g of carbon monoxide react to completion with 10g of hydrogen gas?
 - A. 5 g
 - B. 7 g
 - C. 16 g
 - D. 24 g

Stoichiometry

Answers and Explanations

1. B

The atomic weight of carbon is 12.0u, and the atomic weight hydrogen is 1.0u. Rounding to the whole number value, the molecular weight of C_2H_6 is 30g/mol.

$$MW = \frac{30 \text{ g}}{\text{mol}}$$

A real key to stoichiometric problem solving is to see a molecular weight as a conversion factor. A conversion factor is a variation on the number 1. $30g C_2H_6$ is the same thing as 1 mol. You can always turn a conversion factor upside down.

1 mol 30 g

Now it's just the simple matter of converting the mass of C_2H_6 given in the problem into moles.

$$\left(\frac{1 \text{ mol}}{30 \text{ g}}\right) 0.6 \text{ g} = \left(\frac{6 \times 10^{-1}}{3 \times 10^{1}}\right) \text{ mol}$$
$$= 2 \times 10^{-2} \text{ mol}$$

2. B

With the atomic weights of bromine (79.9u), carbon (12.0u), and hydrogen (1.0u), we have the molecular weights of Br_2 (160g/mol) and acetylene, which is C_2H_2 (26g/mol). We know the stoichiometric ratios of the reagents as they comprise the final compound. A big part of stoichiometrical problem solving is to think on the page through the conversion factors. Lay it out and convert grams Br_2 into moles Br_2 into moles $C_2H_2Br_4$ into moles C_2H_2 into grams C_2H_2 . Use mental math wherever you can, ie.. 500 ÷ 160 ~ 3.

$$500g \operatorname{Br}_{2} \left(\frac{1 \operatorname{mol} \operatorname{Br}_{2}}{160 \operatorname{g} \operatorname{Br}_{2}}\right) \left(\frac{1 \operatorname{mol} \operatorname{C}_{2} \operatorname{H}_{2} \operatorname{Br}_{4}}{2 \operatorname{mol} \operatorname{Br}_{2}}\right) \left(\frac{1 \operatorname{mol} \operatorname{C}_{2} \operatorname{H}_{2}}{1 \operatorname{mol} \operatorname{C}_{2} \operatorname{H}_{2} \operatorname{Br}_{4}}\right) \left(\frac{26 \operatorname{g} \operatorname{C}_{2} \operatorname{H}_{2}}{1 \operatorname{mol} \operatorname{C}_{2} \operatorname{H}_{2}}\right)$$
$$= 41 \operatorname{g} \operatorname{C}_{2} \operatorname{H}_{2}$$

3. C

Let conversion factors unroll it, The answer choices are well spaced. Use mental math $(35.5 \div 72.6 \sim \frac{1}{2})$. Go from grams to moles and then with Avogadro's number from moles to atoms.

$$35.5g \text{ Ge-}\left(\frac{1 \text{ mol}}{72.6 \text{ g-Ge}}\right) \left(\frac{6.02 \times 10^{23} \text{ atoms}}{\text{ mol}}\right) = 2.94 \times 10^{23} \text{ atoms}$$

4. C

A chemical equation needs to be balanced to follow the law of conservation of mass. The equation is balanced when the moles of elements in the reactants side is equal to that of the products side. There is no real secret to balancing chemical equations. It's a process of trial and error.

$$6HCl + 2Cr \longrightarrow 2CrCl_3 + 3H_2$$

5. C

With the atomic weights of carbon (12.0u), chlorine (35.5u), and hydrogen (1.0u), for the *empirical formula* C_2 ClH, we have a *formula weight* of 60.5u.

On the mass spec we see a cluster of peaks near 180u. The reason we don't see a single obvious molecular peak is that there are two stable isotopes of chlorine, ³⁵Cl (75.77%) and ³⁷Cl (24.23%). The relative abundance of these two is why chlorine has a standard atomic weight of 35.45.

Given the molecular peaks clustered just above 180u, the molecular weight of our compound must be 181.5 and the *molecular formula* of our compound must be $C_6Cl_3H_3$.

6. A

Empirical formula from percent composition is a classic Chem 101 problem. The first step is to assume you have 100g of the substance. Then you determine how many moles of each component that represents. Then for the subscripts you figure out the simplest whole number ratio among the moles of components.

$$39 \, \text{gC} \left(\frac{1 \, \text{mol}}{12.0 \, \text{gC}} \right) = 3.3 \, \text{mol}$$

$$16\text{g H} \left(\frac{1 \text{ mol}}{1.0 \text{ g H}}\right) = 16.0 \text{ mol}$$

$$45g N \left(\frac{1 \text{ mol}}{14.0 \text{ g N}}\right) = 3.2 \text{ mol}$$

The simple whole number ratio is 1:5:1, so the correct empirical formula is CH_5N .

7. D

Heating the hydrate drives off the water. The molecular weight of magnesium sulfate (MgSO₄) is 120.4 g/mol. The molecular weight of water is 18.0 g/mol. To determine *n* in the expression MgSO₄-nH₂O from the given information, we can construct and solve the following equation.

$$\frac{120.4}{120.4 + n \, 18.0} = 0.49$$
$$n = 7$$

8. B

Two moles each of H_2O and CO_2 were produced in the combustion reaction. We know then that four moles of hydrogen and two moles of carbon were consumed. How much oxygen reacted from the air? We do know the mass of the original sample. If we subtract out the weight of four moles of hydrogen and two of carbon, we are left with 16 grams of oxygen, or one mole.

9. A

From the reaction it can be seen that one mole of acetylene is produced for every two moles of water consumed. Remember that one ml of water equals one gram, so 18 ml would equal one mole. Therefore, 0.5 moles (13g) of acetylene is produced.

10. B

If *n* equals the number of carbons in an unbranched alkane, 2n + 2 equals the number of hydrogens. Therefore, we can express the stoichiometry of the combustion reaction as follows:

$$C_n H_{2n+2} + (3n+1)/2 \ 0_2(g) \longrightarrow nCO_2(g) + (n+1)H_2O(g)$$

One mole of ideal gas at STP occupies 22.4 liters, so 157 L gas equals seven moles of gas. For *n* moles of CO_2 plus n + 1 moles of H_2O to equal 7, *n* must equal 3.

11. B

Conversion factors unfold it for you and give you the atomic weight of the metal, Ru (101.07u). After laying out the conversion factors, use mental math to see atomic weight is very close to 100 g/mol.

$$\left(\frac{6.75 \text{ g X}}{1.6 \text{ g O}}\right)\left(\frac{16 \text{ g O}}{\text{mol O}}\right)\left(\frac{3 \text{ mol O}}{2 \text{ mol X}}\right) = \left(\frac{101 \text{ g X}}{\text{mol X}}\right)$$

12. C

The first step is to write out the balanced reaction.

$$CO + 2H_2 \longrightarrow CH_3OH$$

The stoichiometry dictates that 1 mol CO reacts with 2 mol H_2 to form 1 mol CH₃OH, but the amounts of our reagents in the vessel aren't at these molar ratios.

$$14 \text{ g CO} \left(\frac{1 \text{ mol}}{28 \text{ g}}\right) = 0.5 \text{ mol CO}$$
$$10 \text{ g H}_2\left(\frac{1 \text{ mol}}{2 \text{ g}}\right) = 5 \text{ mol H}_2$$

Instead of a 1:2 molar ratio between CO and H_2 , what's actually present is a 1:10 ratio. We have H_2 in excess. This means that CO is the *limiting reagent*. It will dictate the amount of CH₃OH per the stoichiometry. If 0.5 mol CO are consumed, 0.5 mol CH₃OH will form, or 16 g (MW CH₃OH = 32 g/mol).

Thermochemistry Practice Items

- 1. 500 kJ of heat flow from a system occurs into the environment at the same time the system is expanding, performing 250 kJ of work on the surroundings, what is the change in the internal energy of the system?
 - **A.** 750 kJ
 - **B.** 250 kJ
 - **C.** + 250 kJ
 - **D.** + 750 kJ
- 2. The amount of heat required to increase the temperature of 1 g of water by 1°C equals
 - **A.** 1 kcal
 - **B.** 4.18 cal
 - **C.** 4.18 J
 - **D.** 1 J
- **3.** Dulong and Petit's law states that the molar heat capacity of many solid elements is approximately 25 J K⁻¹ mol⁻¹. A laboratory scientist working to identify an unknown metal has measured its specific heat, obtaining a value of 0.20 J K⁻¹ g⁻¹. From other tests, he believes the element to be one among the following list. Which is it?
 - A. selenium (AW 78.96 u)
 - **B.** tellurium (AW 127.60 u)
 - **C.** tungsten (AW 183.84 u)
 - **D.** bismuth (AW 208.98 u)

- 4. A positive value of ΔH for a reaction carried out at constant pressure means that:
 - **A.** Heat is given off to the environment during the reaction.
 - **B.** The internal energy of the substance has increased.
 - **C.** The reaction is exothermic.
 - **D.** Heat is absorbed from the environment during the reaction.
- 5. Within an insulated flask, 20g of an alloy at 80°C is dropped into 100ml of water at 28°C. The final temperature is 30°C. What is the specific heat of the alloy?
 - **A.** 0.13 cal g^{-1} °C
 - **B.** 0.20 cal g^{-1} °C
 - **C.** $0.25 \text{ cal } \text{g}^{-1} \circ \text{C}$
 - **D.** 0.50 cal g^{-1} °C
- **6.** Which of the following standard molar enthalpies of formation is not zero?
 - **A.** $O_2(g)$
 - **B.** Hg (l)
 - C. C (graphite)
 - **D.** CH₄
- 7. Carbon and oxygen react to give carbon dioxide. Reacting 8.98 g C(s) with 18.42 g $O_2(g)$ at 1 atm pressure and 298K releases -226 kJ of heat to the surroundings. What is the standard enthalpy of formation of CO₂(g)?
 - **A.** -226 kJ mol⁻¹
 - **B.** -299 kJ mol⁻¹
 - **C.** -393 kJ mol⁻¹
 - **D.** -452 kJ mol⁻¹

8. Two ways pure carbon may be combusted are as follows:

C (graphite) +
$$O_2(g) \longrightarrow CO_2(g)$$

 $\Delta H = -393.5 \text{ kJ mol} -1$

C (graphite) + $1/2 O_2(g) \longrightarrow CO(g)$ $\Delta H = -110.5 \text{ kJ mol}-1$

What is the enthalpy change involved in reacting one mole of carbon monoxide with oxygen to form carbon dioxide?

A.	−172.5 kJ
B.	–283.0 kJ
C.	–504.0 kJ
D.	–566.0 kJ

9. Which of the following statements is true about the following exothermic reaction carried out to completion at 300K and 1kPa pressure?

 $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$

- **A.** The decrease in internal energy is greater than the enthalpy change.
- **B.** The magnitude of the internal energy change is less than the magnitude of the enthalpy change.
- **C.** The enthalpy change equals the loss of internal energy.
- **D.** The enthalpy decreased while internal energy increased.

10. Elemental phosphorus can exist in several allotropes; the most common of which are white and red solids. The white form is the standard state. White phosphorus exists as molecules made up of four atoms in a tetrahedral structure. White phosphorus reacts with oxygen and water to form phosphoric acid:

 P_4 (white) + 5 O_2 + 6 $H_2O \longrightarrow 4H_3PO_4$

At 298K and 1 atm, the enthalpy change of the above reaction equals:

- **A.** the standard enthalpy of formation of phosphoric acid minus the standard enthalpy of formation of water.
- **B.** the sum of the bond dissociation energies of products and reagents.
- **C.** four times the standard enthalpy of formation of phosphoric acid minus six times the standard enthalpy of formation of water.
- **D.** the bond dissociation energy of phosphoric acid.
- **11.** Which of the following statements does not directly follow from or lead to Hess' Law?
 - I. The enthalpy change for a reaction may depend on whether a one step or a five step process is utilized.
 - II. The enthalpy change of a reaction equals the standard enthalpies of the products minus the standard enthalpies of the reagents.
 - III. Enthalpy is a state function.
 - **A.** I
 - **B.** I and III
 - C. II and III
 - **D.** I, II and III

Thermochemistry

12. The table below provides the heat capacities of ice, liquid water, and steam as well as the heats of transformation for melting and boiling water (P = 1atm).

c_{ice} (cal/g ·°C)	Latent Heat of Fusion (cal/g)	C _{water} (cal/g ⋅°C)	Latent Heat of Vaporization (cal/g)	C _{steam} (cal/g ⋅°C)
0.5	80	1	540	0.48

For which of the choices below does the enthalpy change have the greatest difference with internal energy change?

- A. heating 1 mole of ice at 1atm pressure from -150°C to -50°C
- **B.** melting 1 mole of ice at 1atm pressure at 0°C
- C. heating 1 mole of liquid water from 0°C to 100°C
- **D.** vaporizing 1 mole of water at 100°C

13. Given these bond energies:

H–H	(435 kJ/mol)
Br–Br	(192 kJ/mol)
H–Br	(368 kJ/mol)

Which is following would be the best estimate of the enthalpy change of the following reaction?

 $H_{2}(g) + Br_{2}(g) \longrightarrow 2HBr(g)$

- **A.** -26 kJ
- **B.** -109 kJ
- **C.** +109 kJ
- **D.** +259 kJ

The following passage pertains to questions 14 - 16.

A bomb calorimeter consists of a strong steel container, called a bomb, in which reactants are placed and then immersed in an insulated bath holding a known quantity of water. A heater wire in the bomb is often used to set the reaction off.



After the reaction has occurred and thermal equilibrium is reached within the calorimeter, the entire system will be at a higher temperature. By carefully measuring the temperature of the water before and after reaction, the quantity of heat evolved by the chemical reaction can be computed.

In a particular experiment a researcher compressed 0.2 mol of H_2 and 0.1 mol of O_2 into a 0.5 liter bomb. The bomb was then immersed in the water of a calorimeter. The heat capacity of the entire calorimeter apparatus including water was 10850 cal/°C. A reaction was set off which proceeded to completion. Before the reaction, the temperature of the water was 25.00°C. After the reaction, the temperature was measured to be 26.25°C.

- **14.** Which of the following is the closest value to the pressure in the bomb if it were measured prior to reaction ignition?
 - **A.** 1.2 atm
 - **B.** 14 atm
 - **C.** 65 atm
 - **D.** 150 atm

- **15.** What is the magnitude of heat flow that occurred into the water bath and calorimeter apparatus in the reaction described in the passage?
 - **A.** 14 kJ
 - **B.** 57 kJ
 - **C.** 109 kJ
 - **D.** 285 kJ
- 16. Suppose that 2 moles of hydrogen atoms were injected into a bomb calorimeter. The hydrogen atoms react to form 1 mol of H_2 . Heat flow occurs from the system into the surrounding water bath and calorimeter apparatus. This heat flow would be equal in magnitude to
 - **A.** the enthalpy change of the reaction.
 - **B.** the standard enthalpy of formation of H_2 .
 - C. the internal energy decrease in the system.
 - **D.** H_2 bond dissociation energy.

Thermochemistry

Answers and Explanations

1. A

A thermodynamic system has two means of exchanging energy with its surroundings, heat flow and pressure-volume work. Heat flow, Q, is the transfer of thermal energy due to temperature difference. Work, W, is macroscopic energy transfer between the system and its surroundings that occurs through force exerted along the direction of a displacement. In a thermodynamic system, work manifests as the exertion of pressure through a change in volume. The First Law of Thermodynamics expresses the principle of energy conservation for thermodynamic systems. The total internal energy change of the system can be determined as an accounting of the heat flow and the work.

$$\Delta U = Q - W$$

$$= Q - P^* \Delta V$$

$$\Delta U = internal energy chan
Q
= heat flow
W
= macroscopic work
P^* = constant pressure
\Delta V = volume change$$

Heat flowing from the system into the surroundings costs the system internal energy, so the system lost 500 kJ of internal energy due to the heat flow. Additionally, expansion, in which the system performs pressure-volume work on the surroundings, also costs the system. It loses an additional 250 kJ of energy due to the thermodynamic work.

2. C

One calorie is the amount of heat required to increase the temperature of 1 g of water by 1°C. One calorie equals 4.18 J.

$$1 \text{ calorie} = 4.18 \text{ joules}$$

3. A

The specific heat tells you how many joules (or calories) of heat flow are required to raise a *gram* of a substance by one degree. The molar heat capacity tells you the heat flow to raise a *mole* of a

substance by one degree. It's not difficult to see then that one would multiply specific heat by molecular weight to convert it to molar heat capacity. For the purpose of our problem then we could do this in reverse and divide the molar heat capacity by the specific heat to determine molecular weight.

$$\frac{25 \text{ J K}^{-1} \text{ mol}^{-1}}{0.20 \text{ J K}^{-1} \text{ g}^{-1}} = 125 \text{ g mol}^{-1}$$

4. D

As long as pressure is constant, any change in the enthalpy of a system will equal the heat flow, so a positive enthalpy change means that heat is absorbed by the system. The concept of the equivalence of enthalpy change and heat flow (as long as pressure is constant) is the foundation of thermochemistry. It allows us to describe heat flow in terms of the change in a state function. Enthalpy change is path independent.

Note with regard to choice 'B' that enthalpy change equals internal energy change only if the volume of the system remains constant (and thus no thermodynamic work is performed).

5. B

The heat flow to or from an object changing temperature equals the product of the mass of the object, the specific heat of its material, and the temperature change.

$$Q = m c \Delta T$$

The amount of heat flowing from the alloy will equal the heat flowing into the water.

$$(20 \text{ g}) c (80^{\circ}\text{C} - 30^{\circ}\text{C}) =$$

(100 g)(1 cal g⁻¹°C⁻¹)(30°C - 28°C)

$$(20 \text{ g}) c (80^{\circ}\text{C} - 30^{\circ}\text{C}) = 200 \text{ cal}$$

$$c = 0.2 \text{ cal } \text{g}^{-1} \text{°C}^{-1}$$

6. B

For all but methane, the elements are in their standard states. The value is zero for standard enthalpy of formation. There is no heat flow to form these from their standard states. That's what they are.

7. B

In our reaction vessel, we start with approximately $\frac{3}{4}$ of a mole of carbon. We react this with a bit more than $\frac{1}{2}$ of a mole of O₂. However, the stoichiometry of the reaction calls for a 1:1 ratio for both reagents to be completely consumed, so O₂ is going to be a limiting reagent in this case. it will dictate the amount of CO₂ formed. We see we only form somewhat more than half a mole of CO₂. Because we are forming somewhat more than half a mole of CO₂, the 226 kJ liberated represents somewhat more than half of the standard enthalpy of formation of CO₂, which must be 393 kJ mol⁻¹, the only value somewhat less than twice 226 kJ.

8. B

Hess' Law allows us to imagine a path for the reaction of carbon monoxide with oxygen to form carbon dioxide. First, we run the CO formation reaction in reverse ($\Delta H = +110.5 \text{ kJ}$) to convert a mole of carbon monoxide into graphite and oxygen. We can then react the graphite and oxygen to form a mole of CO₂ ($\Delta H = -393.5 \text{ kJ}$).

9. B

When our reaction has gone to completion, the system will have changed from 3 moles of gas to 2 moles of gas. The volume decreased. The system is losing enthalpy in the pressure-volume product in addition to the loss of internal energy (H = U + PV). From the 1st law point of view, the surroundings are performing work on the system as it compresses. This energy adds to the heat flow out. The enthalpy decrease (heat flow) is greater than the internal energy decrease.

10. C

The standard enthalpy of formation of a compound represents the enthalpy change involved in forming that compound from its constituent elements in their standard states. The standard state of an element is the agreed upon most common pure form of the element. For example, the standard state of oxygen is O_{γ} gas. The standard state of carbon is C(graphite). Using standard enthalpies of formation to compute the enthalpy change of a reaction is a useful technique in thermochemistry because the standard enthalpy of formation of almost every compound of interest will have been experimentally determined and recorded. This allows us to construct an imaginary path from the reagents to the products in which we transform the reagents into the standard states (heat flow occurring of minus the standard enthalpy of formation of the reagents) and then form the products (heat flow occurring equal to the standard enthalpy of formation of the products). For a particular reaction you scale the standard enthalpies to reflect the stoichiometry of the reaction. We know that the enthalpy computed in this way will be valid because the enthalpy change doesn't depend on the path (Hess' Law).

11. A

Hess' law states that the total enthalpy change during the complete course of a chemical reaction is the same whether the reaction is made in one step or in several steps. The law is valid because the enthalpy of a chemical system is a state function of the system, so the difference in enthalpy between two states depends on those states, not on the path between the states. This is a fundamental idea of chemical thermodynamics.

Sometimes people say that Hess' Law is that the enthalpy of a reaction equals the standard enthalpy of formation of the products minus the standard enthalpy of formation of the reagents. That isn't Hess' Law, just an important application. Computing the enthalpy change of a reaction in this manner, taking standard enthalpies from a table, is to imagine a stepwise path for the reaction where we have converted the reagents into the standard states of the elements and then converted the standard states into the products. Hess' Law tells us that the enthalpy change we compute will be valid even though the path is imaginary.

12. D

The enthalpy of a system is the sum of the internal energy and the pressure-volume product.

$$H = U + PV$$

If the pressure is constant, a change in the enthalpy will equal the heat flow. It can be helpful to think of the enthalpy as the 'thermal potential' of the system, the things in the system that can change and produce heat flow. The internal energy might decrease and lead to heat flow out of the system, or the system might be compressed, leading to heat flow out. You see the same thing in the 1st law where the heat flow might result from internal energy change or thermodynamic work.

$$Q = \Delta U + W$$

Whether the heat flow (Q or ΔH) will equal the internal energy change ΔU will depend on whether or not thermodynamic work is occurring. If the volume of the system is changing, the heat flow and the internal energy change will not be equal. Of the choices presented, all except for vaporization are occurring at constant or approximately constant volume, but to vaporize a mole of water it must expand from 18ml in volume (the volume of 18g of liquid water) to approximately 30L in volume (the volume of 1 mole of gas at 100°C). This takes work equal to the change in volume times atmospheric pressure. This work will represent the amount that the heat of vaporization is greater than the internal energy increase of the water.

13. B

Bond energies can give a good estimate of the enthalpy of a reaction. Imagine breaking the reagent bonds (endothermic) to yield two moles each of loose hydrogen and bromine atoms. This requires input of +435 kJ/mol for H₂ and +192 kJ/mol for the Br₂. Now imagine letting the loose hydrogen and bromine atoms fall together to form two moles of HBr molecules (exothermic). Forming the new bonds would liberate 2×-368 kJ/mol. The net enthalpy change for our imaginary pathway would be -109 kJ/mol.

14. B

The ideal gas law gives us a straightforward path. (Ideally you know *R* in these two forms, ie. 8.3 J mol⁻¹ K⁻¹ and .082 L-atm mol⁻¹ K⁻¹.)

$$PV = nRT \qquad P = \frac{nRT}{V}$$

$$P = \frac{(0.3 \text{ mol}) (0.08 \text{ L atm mol}^{-1}\text{K}^{-1}) (298 \text{ K})}{(0.5 \text{ L})}$$

$$P = 14.3 \text{ atm}$$

15. C

The heat flow that occurred is simply the product of the heat capacity of the water bath and apparatus and the temperature change ($\Delta T = 26.25^{\circ}$ C – 25.00°C = 1.25°C). Remember to convert to joules!

$$Q = (10850 \text{ cal/}^{\circ}\text{C})(1.25^{\circ}\text{C}) = 13560 \text{ cal}$$

(14720 cal)(4.18 J/cal) = 56700 J

16. C

Choice 'A' is incorrect. The heat flow occurring here does not equal the enthalpy change for the reaction. Enthalpy (H = U + PV) is a state function whose change will equal the heat flow, Q, only if constant pressure is maintained. This is one of the reasons so many chemistry problems have the statement 'the reaction was carried out at STP' Constant pressure is necessary for ΔH to equal the heat flow. Choice 'D' is not correct for the same reason. Bond dissociation energy is the enthalpy change in bond formation under standard conditions. Choice 'C' is correct because the bomb has a fixed volume. There is no thermodynamic work involved, so by the 1st law of thermodynamics the magnitude of heat flow will exactly equal the magnitude of internal energy change.

$$\Delta U = Q - W$$
$$W = 0$$
$$\Delta U = Q$$

States of Matter Practice Items

- 1. As a researcher decreases the volume of helium gas at constant temperature
 - Α. heat flow occurs into the gas.
 - B. the temperature increases.
 - С. the temperature decreases.
 - the pressure increases. D.
- 2. Approximately how many atoms are in 1 liter of helium at STP?
 - 2×10^{19} A.
 - **B**. 3×10^{23}
 - C. 6×10^{24}
 - 1×10^{26} D.
- 3. Which of the following statements about gases is **untrue**?
 - Α. An equal number of molecules occupies equal volumes of two ideal gases at the same temperature an pressure.
 - **B**. The internal energy of an ideal gas depends only upon the average kinetic energy of its particles.
 - C. An ideal gas would be predicted to occupy zero volume at absolute zero.
 - D. The pressure of real gases will tend to be slightly greater than predicted by the ideal gas law.
- For a mixture of gases within a vessel of 4. fixed dimensions the volume of each component is
 - proportional to its mole fraction in the Α. gaseous mixture
 - **B**. equal
 - С. dependent on the temperature
 - D. proportional to its partial pressure

The following passage pertains to questions 5 - 9.

An apparatus is used to collect a sample of a gaseous substance in the laboratory. In the initial state the flask is completely filled with water. The atmospheric pressure on the water in the surrounding tank enables the water in the flask to be suspended. Gas is collected by displacing the water in the flask until the state illustrated below is attained, in which the level of the water in the flask equals the level in the tank and the collection is completed.



- 5. At the time collection is completed, which of the following statements is true regarding the pressure of the gas, P_{gas} ?
 - A.
 - P_{gas} equals 760 torr. P_{gas} will be greater than atmospheric **B**. pressure if temperature of the gas is higher than the ambient temperature.
 - C. The ratio of P_{gas} to the atmospheric pressure equals the ratio of their densities.
 - D. $P_{_{\rm gas}}$ equals atmospheric pressure.
- 6. After the collection of gas is first initiated, and the level of water in the flask begins to fall the pressure of the trapped gas
 - is less than 760 torr. Α.
 - **B**. equals 760 torr.
 - is greater than 760 torr. С.
 - D. is decreasing.

- 7. Suppose that the temperature in the laboratory is 33°C (in which case the vapor pressure of water is 37.7 torr.) The gas being collected is argon. What is its approximate mole fraction of argon in the space above the water at the time collection is completed?
 - **A.** 0.05
 - **B.** 0.80
 - **C.** 0.90
 - **D.** 0.95
- 8. Student A begins collecting methane gas (CH_4) in this manner and student B begins collecting propane gas (C_3H_8) . After each has collected one gram of substance
 - A. the gaseous phase in student A's flask has greater volume.
 - **B.** the gaseous phase in student B's flask has greater volume.
 - **C.** the volume of the gaseous phases of both flasks are equal.
 - **D.** the gaseous phase in student A's flask has greater density.
- **9.** Although the atmospheric pressure did not change, the temperature in the laboratory increased between experiments with the same gas.
 - **A.** Fewer moles of gas are collected in the flask than before.
 - **B.** The mole fraction of water vapor in the flask is lower than before.
 - **C.** The volume of the gaseous phase is greater than before.
 - **D.** More than one of the above is correct.

- 10. A manometer is a device used for pressure measurements. An open-end manometer is simply a U-shaped tube containing mercury. One arm of the tube is connected to a system whose pressure is to be measured while the other arm remains open to the atmosphere. Which of the following statements is not necessarily true regarding the monatomic gas in the manometer below if the gas is in thermal equilibrium with its surroundings?
 - **A.** The pressure of the gas is greater than atmospheric pressure.
 - **B.** The density of the gas is greater than the density of the atmosphere.
 - **C.** No net heat flow is occurring between the gas and its surroundings.
 - **D.** The molar heat capacity of the gas is lower than the molar heat capacity of N_2 .



- 11. What volume will 14g of N₂ occupy at 25°C and a pressure of 0.8 atm? (R = 0.0821 liter atm mol⁻¹ K⁻¹)
 - **A.** 1.5 L
 - **B.** 15 L
 - **C.** 25 L
 - **D.** 30 L

- 12. If 100 ml of N_2 at 25°C and a pressure of 200 torr along with 200 ml of O_2 at 25°C and a pressure of 250 torr are introduced in mixture into a 200 ml container, what would be the final pressure of the mixture at 25°C?
 - **A.** 200 torr
 - **B.** 250 torr
 - **C.** 350 torr
 - **D.** 450 torr
- **13.** When a liquid attains such a temperature that its vapor pressure equals the external pressure
 - **A.** the liquid and its vapor achieve a state of dynamic equilibrium.
 - **B.** it melts.
 - C. the cohesive forces in the liquid become weaker than the adhesive forces.
 - **D.** it boils.
- **14.** The phase diagram below is for which substance?
 - A. carbon dioxide
 - **B.** sodium
 - C. water
 - D. argon



15. The van der Waal equation of state describes the deviation of a real gas from ideal gas behavior.

$$\left(\mathbf{P} + \frac{an^2}{\mathbf{V}^2}\right)(\mathbf{V} - nb) = n\mathbf{R}\mathbf{T}$$

What is the physical basis of the constant '*a*' in the van der Waal equation of state?

- A. the attractive forces between molecules of the gas
- **B.** the effective size of the gas particles
- **C.** rotational and vibrational modes of internal energy
- **D.** super-elastic collisions

16. The graph below shows the heating curve for 1 mol of an unknown substance.



From the graph it can be seen that the substance

- A. exhibits the properties of a liquid crystal
- **B.** has a greater heat of fusion than heat of vaporization
- C. undergoes supercooling
- **D.** has a higher molar heat capacity as a gas than as a liquid

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17. Why is the level of mercury lower in a capillary tube than the level outside when the capillary tube is inserted into mercury?



- **A.** Cohesive forces are stronger than adhesive forces in the case of mercury
- **B.** The pressure exerted by the atmosphere is greater within the capillary tube.
- **C.** The high specific gravity of mercury overcomes the cohesive forces.
- **D.** The vapor pressure of mercury can be established within the capillary tube but not on the open surface.
- 18. Dry ice, the solid form of carbon dioxide, is a
 - A. covalent network solid
 - **B.** molecular solid
 - C. ionic solid
 - **D.** atomic solid
- **19.** Which of the following crystal structures is capable of greatest density?
 - A. face-centered cubic structure
 - **B.** body-centered cubic structure
 - C. primitive cubic structure
 - **D.** all can be equally dense

- **20.** Potassium metal crystallizes in a body-centered cubic lattice. How many potassium atoms are contained within one unit cell?
 - **A.** 1
 - B. 2C. 5
 - **D.** 9

States of Matter

Answers and Explanations

1. D

Boyle's Law governs isothermal (constant temperature) transformations. At constant temperature the pressure of an ideal gas sample is inversely proportional to its volume, i.e. PV = constant. If the volume of a particular sample of gas is halved the pressure doubles (if constant temperature is maintained).

The pressure increases in an isothermal compression not because the gas particles are moving more vigorously but because they have become more crowded, and a surface area in contact with the compressed gas experiences more collisions with gas particles in a given amount of time.



2. B

An ideal gas occupies 22.4 L at STP. A real gas will not deviate too greatly from this, especially a noble gas like helium.

$$1 L \frac{(1 \text{ mol})}{(22.4 \text{ L})} \frac{(6.02 \times 10^{24} \text{ molecules})}{(1 \text{ mol})}$$
$$\sim \frac{6 \times 10^{24} \text{ molecules}}{2 \times 10^{1}}$$

~
$$3 \times 10^{23}$$
 molecules

3. D

As can be seen in the Van der Waals equation of state, the pressure of real gases will tend to be slightly *lower* than predicted by the ideal gas law.

$$\left(P + \frac{a n^2}{V}\right)\left(V - n b\right) = n R T$$

a and b are specific constants for each gas.

4. B

A gas takes the volume of its container, so each component has an equal volume, the volume of the container.

5. D

The pressure in a static fluid is the same everywhere in the fluid at the same level, even when the pressure is due to different causes. In other words, the water in contact with the trapped gas is at the same level as the water in contact with the atmosphere. Therefore, the pressure of the gas must be equal to atmospheric pressure. Note that choice 'A' is incorrect. Even though 760 torr is equal to 1 standard atmosphere (1 atm), the actual atmospheric pressure will be somewhat greater or less depending on the weather.

6. A

The figure below depicts the apparatus after collection of gas is first initiated.



Because the pressure in a static fluid is the same everywhere at the same level, P_x must equal P_{atm} . Furthermore, P_x is at a greater depth in the fluid than the surface of the fluid in contact with the gas, which is at the same pressure as the gas. Therefore, $P_x < P_{gas}$.

7. D

At the time collection is completed, the water in contact with the trapped gas is at the same level as the water in contact with the atmosphere. Therefore, the total pressure of the gas above the water must be equal to atmospheric pressure. However, the gas above the water is a mixture of argon and water vapor. The partial pressure of the water vapor is equal to its vapor pressure. At 33°C this is 37.7 torr.

Dalton's Law of Partial Pressures tells us that the total pressure of a gaseous mixture equals the sum of the partial pressures of the gaseous components of the mixture. The total pressure is equal to the atmospheric pressure, 760 torr more or less, so the partial pressure of argon is approximately 722 torr.

The partial pressure of any gas in a mixture is the total pressure multiplied by the mole fraction of that gas. Another way to say this is that the partial pressure fraction of a gas is equal to its mole fraction. The mole fraction of argon is 0.95.

8. A

Rearranging the ideal gas law we can see that if pressure and temperature are the same, the volume will be directly proportional to the number of moles of a gas. It's the number of particles that determines the macrosate behavior of a gas, in other words, not the size of the individual particles.

$$PV = nRT$$
$$V = n \frac{RT}{P}$$

Student A collected a gram of methane. Student B collected a gram of propane. Because the molecular weight of methane is lower than that of propane, a gram of methane will have more particles.

With fewer grams per mole, there are more moles per gram. The volume of 1 gram of methane will be greater than 1 gram of propane.

9. A

Collection is completed when the level of the water in the flask equals the level in the tank. The volume is the same in both experiments, and the pressure of the gas equals atmospheric pressure. To have the same pressure and volume at a greater temperature, there must be fewer moles of gas.

10. B

Choice 'B' is not necessarily true. The gas is the same temperature as the atmosphere, and given the current state of the manometer, the gas must have a greater pressure than atmospheric pressure. For it to have a greater pressure at the same temperature, it must have a greater *molar density* than the atmosphere. At the same temperature molar density goes up with pressure.

$$\frac{n}{V} = \frac{P}{RT}$$

However, if the molecular weight of the gas is significantly less than the average molecular weight of the N_2 and O_2 comprising the atmosphere (if the gas were helium or neon, for example) its density (mass per unit volume) might actually be less than the density of the atmosphere despite the fact that its molar density is greater.

11. B

This is a straightforward ideal gas law problem, but first we need to compute the moles of N_2 .

$$14 \text{ g} \quad \frac{1 \text{ mol}}{28 \text{ g}} = 0.5 \text{ mol}$$
Now we can compute the volume.

$$PV = nRT$$

$$V = \frac{nRT}{P}$$

$$V = \frac{(0.5 \text{ mol})(0.08 \text{ liter atm mol}^{-1} \text{ K}^{-1})(298\text{K})}{(0.8 \text{ atm})}$$

$$V = 14.9 \text{ L}$$

12. C

It helps us to find a simple path for this problem to think about how in the ideal gas law a pressure-volume product corresponds to a number of moles of gas at a certain temperature.

$$PV = nRT$$

This means that the sum of the pressure-volume products of the two gases before admixture will equal the sum of their moles times the temperature, and, furthermore, will equal the pressure-volume product of he mixture.

 $P_{\text{mixture}}(200 \text{ ml}) = (200 \text{ torr})(100 \text{ ml}) + (250 \text{ torr})(200 \text{ ml})$

 $P_{\text{mixture}} = \frac{(200 \text{ torr})(100 \text{ ml}) + (250 \text{ torr})(200 \text{ ml})}{(200 \text{ ml})}$ $P_{\text{mixture}} = 350 \text{ torr}$

13. D

The boiling point of a liquid is the temperature at which its vapor pressure is equal to the pressure of the gas above it, the external pressure, which is usually atmospheric pressure. The normal boiling point is the temperature at which the vapor pressure of a liquid becomes equal to 1 atm pressure. In comparing molecules of the same size, if the intermolecular forces are small, the liquid has a high vapor pressure and a low boiling point. Conversely, liquids in which the intermolecular forces are strong will have a low vapor pressure and a high boiling point.

14. C

It is a practically unique characteristic of water that its solid phase is less dense than its liquid phase. This causes the equilibrium to shift from the greater volume solid phase towards the lower volume liquid phase at high pressures. Unlike with other substances, the line separating the solid and liquid phases on the phase diagram of water leans leftward.

15. A

The Van der Waals equation of state adjusts the ideal gas law based on the deviation of real gas behavior from ideal gas behavior. The addition to the pressure term in the ideal gas law of an^2/V^2 in the Van der Waals equation of state accounts for the fact that real gas molecules do in fact interact with each other and therefore show different compressibility than ideal gases. Because of intermolecular interaction the pressure is a little bit lower than one would expect based on ideal gas behavior. The value of the constant *a* depends on the gas.

16. C

The challenge in this question is to recognize the narrative for the substance as heat flows out.



Supercooling is the cooling of a liquid below its freezing point without it becoming solid.

17. A

In this context we refer to the attractive forces between molecules of the same substance as cohesive forces. The forces between molecules of different substances are called adhesive forces. In case of mercury, the cohesive forces are stronger than the adhesive forces. As a result mercury detaches from the glass surface and its level goes down in the capillary tube.

18. B

In a molecular solid the positions in the lattice are occupied by molecules. A molecular solid is held together by intermolecular forces.

19. A

Even though crystal structure is not mentioned on the AAMC outline, we've included a couple of questions to provide a very simple orientation because it would not be out of character mention of these ideas within a passage, even though there would not be an explicit penalty for a lack of foreknowledge.

The face-centered cubic structure is also called cubic closest packing and can utilize seventy-four percent of available space.



20. B

The body centered cubic unit cell has an atom at each of its eight corners, which it shares with eight other unit cells ($8 \times \frac{1}{8}$ atom = 1 atom). Additionally there is an atom in the center of the cell, so the total is 2 atoms per unit cell.



Chemical Thermodynamics and Equilibrium Practice Items

- 1. Chemical equilibrium occurs when
 - I. the rate of the forward reaction equals the rate of the reverse reaction.
 - II. the concentrations of products and reactants attain steady state values.
 - III. heat flows between the system and environment are reversible.
 - **A.** I
 - **B.** I and III
 - C. II and III
 - **D.** I, II and III
- 2. Which of the following is the proper expression of K_c for the following reaction?

 $4NH_3(g) + 5O_2(g) - 4NO(g) + 6H_2O(g)$

$$\mathbf{A.} \quad \frac{\left[\mathsf{NH}_3\right]\left[\mathsf{O}_2\right]}{\left[\mathsf{NO}\right]\left[\mathsf{H}_2\mathsf{O}\right]}$$

- B. $\frac{4[NO] \ 6[H_2O]}{4[NH_3] \ 5[O_2]}$
- $\textbf{C.} \quad \frac{\left[\textbf{NO}\right]^{4}\left[\textbf{H}_{2}\textbf{O}\right]^{6}}{\left[\textbf{NH}_{3}\right]^{4}\left[\textbf{O}_{2}\right]^{5}}$
- **D.** $\frac{[NH_3]^4 [O_2]^5}{[NO]^4 [H_2O]^6}$

- **3.** The reaction of sulfur dioxide with oxygen occurs according to the following stoichiometry:
 - $3SO_2(g) + O_2(g) \implies 2SO_3(g)$ $\Delta H = -197.8 \text{ kJ mol}^{-1}$

At 1000°C and 0.3 atm, the equilibrium constant, K_p , is equal to 3.42. Which of the following strategies would be likely to increase the equilibrium yield of sulfur trioxide?

- I. Increasing the pressure of the reaction vessel
- II. Introducing a catalyst
- III. Heating the reaction vessel further
- A. I only
- **B.** I and III
- C. II and III
- **D.** I, II and III
- 4. Which of the following will lead to an *increase* in the equilibrium constant?
 - I. Increasing the temperature of an endothermic reaction
 - II. Increasing the pressure of a reaction vessel where products represent fewer moles of gas than the reagents
 - III. Introducing a catalyst
 - A. I only
 - **B.** I and II
 - C. II and III
 - **D.** I, II and III

5. The equilibrium constant under standard conditions for the reaction of SO₂ with O₂ to form SO₃, $K_c = 1.5 \times 10^{-1} M^{-1}$

 $2SO_{2}(g) + O_{2}(g) \implies 2SO_{3}(g)$

If 0.01 mol of each of the three gases are present along with argon in a 1 liter container at STP, which of the following is occurring?

- **A.** The forward reaction occurs at a higher rate than the reverse reaction.
- **B.** The reverse reaction occurs at a higher rate than the forward reaction.
- **C.** The reaction is at equilibrium.
- **D.** Pressure is increasing in the container.
- 6. Which statement below about standard free energy change, ΔG° , is **untrue**?
 - A. If ΔG° for a reaction is large and positive, the equilibrium constant, *K*, is very small.
 - **B.** If ΔG° for a reaction is large and negative, *K* is very large.
 - C. If ΔG° is large and negative, the reaction will be spontaneous forward for all concentrations of reagents and products.
 - **D.** ΔG° may be negative even with a positive standard enthalpy change ΔH° .
- 7. Cyclohexanol inter-converts between axial and equatorial conformations. At 25°C, about 90% exists in the equatorial form with the remainder in the axial form. What is the approximate standard free energy change for with the transformation from equatorial to axial cyclohexanol?
 - **A.** -2 kJ mol⁻¹
 - **B.** 0.5 kJ mol⁻¹
 - **C.** 2 kJ mol⁻¹
 - **D.** 5 kJ mol^{-1}

8. $CO(g) + H_2O(g) \iff CO_2(g) + H_2(g)$

 $K_c = 4.05$ at 500°C for the above reaction. If 1.0 mole of both carbon monoxide and water vapor are placed in a 2.0 liter container at 500°C, approximately what concentration of carbon monoxide will be in the container at equilibrium?

- **A.** 0.17 M
- **B.** 0.25 M
- **C.** 0.33 M
- **D.** 0.67 M
- **9.** Which of the following is the result when the decomposition of ammonium chloride occurs in an open container at STP?

 $NH_4Cl(s) \iff NH_3(g) + HCl(g)$

- A. Decomposition does not occur.
- **B.** All of the ammonium chloride is eventually consumed.
- **C.** The entropy of the system decreases.
- **D.** The system eventually achieves equilibrium as described by K_p for the decomposition of NH_4Cl at STP.
- **10.** The decomposition of solid ammonium carbamate occurs by the following reaction.

$$(NH_4)(NH_2CO_2)(s)$$
 $2NH_3(g) + CO_2(g)$

When solid ammonium carbamate is introduced into an evacuated flask at 25°C, the total pressure of gas at equilibrium is 0.117 atm. What is the value of K_p at 25°C?

A. 2.4×10^{-4} B. 3.0×10^{-3} C. 3.9×10^{-2} D. 1.2×10^{-1} The following passage pertains to questions 10-15

Sulfur has various allotropic forms. At room temperature, sulfur exists in yellow crystals consisting of S_8 molecules arranged with rhombic symmetry. The melting point of rhombic sulfur is 113°C. At this temperature, however, the liquid sulfur may be recrystallized to form a monoclinic allotrope, the melting point of which is 119°C. These two crystalline forms are pictured below:



The table below provides the values of various thermodynamic functions of rhombic and monoclinic sulfur at various temperatures:

	rhombic sulfur		monoclinic sulfur	
T [K]	$H^{\left[\frac{kJ}{mol}\right]}$	$S^{\left[\frac{\mathrm{J}}{\mathrm{K} \mathrm{mol}} \right]}$	$H^{\left[rac{kJ}{mol} ight]}$	$S^{\left[\frac{\mathrm{J}}{\mathrm{K} \mathrm{mol}} \right]}$
300	5.5	39.0	5.9	40.1
310	5.7	39.5	6.1	40.6
320	5.9	40.0	6.3	41.1
330	6.1	40.5	6.5	41.6
340	6.3	41.0	6.7	42.1
350	6.5	41.5	6.9	42.6
360	6.7	42.0	7.1	43.1
370	6.9	42.5	7.3	43.6
380	7.1	43.0	7.5	44.1

- **11.** S_8 molecules are held within the crystal lattice of elemental sulfur by
 - A. strong nuclear forces
 - **B.** dipole-dipole interactions
 - C. Van der Waals forces
 - **D.** covalent bonds

- **12.** How many sulfur atoms are in an orthorhombic sulfur unit cell?
 - **A.** 6
 - **B.** 8
 - **C.** 32
 - **D.** 64

- **13.** What is the approximate specific heat of rhombic sulfur?
 - **A.** 0.8 J g^{-1} K⁻¹
 - **B.** 2.0 J $g^{-1} K^{-1}$
 - C. $4.8 \text{ J g}^{-1} \text{ K}^{-1}$
 - **D.** 20 J mol⁻¹ K⁻¹

- **14.** Which of the following is the correct interpretation of the fact that rhombic sulfur is the lower temperature form and monoclinic sulfur is the higher temperature form?
 - I. Addition of heat shifts equilibrium to favor the endothermic process.
 - II. At higher temperatures the change in free energy from the rhombic to the monoclinic form is positive.
 - III. Enthalpy change favors the rhombic but the entropy change favors the monoclinic.
 - **A.** I
 - **B.** III
 - C. I and III
 - **D.** I, II, and III

Cheical Thermodynamics

- **15.** Which is the best explanation for why rhombic sulfur possesses a lower melting point (113°C) than monoclinic sulfur (119°C)?
 - **A.** In that temperature range, rhombic sulfur has greater free energy.
 - **B.** In that temperature range, monoclinic sulfur has less entropy.
 - **C.** In that temperature range, monoclinic sulfur has greater free energy.
 - **D.** In that temperature range, rhombic sulfur has greater enthalpy.
- **16.** What is the approximate value of the temperature at which, if you cooled molten sulfur, there would be an equal probability of obtaining by crystallization either rhombic or monoclinic sulfur?
 - **A.** 310 K
 - **B.** 335 K
 - **C.** 365 K
 - **D.** 400 K

Chemical Thermodynamics and Equilibrium

Answers and Explanations

1. D

All are characteristics of equilibrium.

2. C

Choice 'C' represents the proper expression of K_c , the equilibrium constant for this reaction. The equilibrium constant is the particular value of the reaction quotient, Q, that reflects the concentrations at equilibrium. Note that stoichiometric coefficients become exponents in reaction quotients and equilibrium constants. You can tell the exponents from the stoichiometry. This is in contrast to rate expressions in chemical kinetics, where the exponents must be found experimentally.

3. A

Le Chatelier's principle tells us that if you disturb a system at equilibrium the system will respond in such a way that opposes the disturbance. One application of the principle is that when the pressure is increased for a chemical reaction, the equilibrium will shift to favor the direction that leads to lower volume. The most common framework in which this applies is a reaction involving gases in which there is a difference in the number of moles of gas between reagents and products. Increasing the pressure will cause the equilibrium to shift to favor formation of the fewer moles of gas. In the case of our reaction, there are four moles of gas on the reagent side and two moles of gas on the product side, so increasing pressure will lead to the formation of more product at equilibrium.

Regarding choice 'II', introducing a catalyst will not increase the equilibrium yield of the reaction (though it may increase the practical yield). A catalyst affects the rate of a reaction not the position of equilibrium. Regarding choice 'III', heating the reaction vessel will not increase the equilibrium yield. One of the situations Le Chatelier's principle helps to predict is what occurs to the position of equilibrium when the temperature of a reaction is changed. When the temperature of a reaction is increased, equilibrium shifts to favor the endothermic direction. As indicated by the negative enthalpy change in the given information, the forward direction of our reaction is exothermic. Therefore, it is the reverse direction, the conversion of products to reagents, which is endothermic and which will be promoted by an increase in temperature.

4. A

Increasing the temperature of an endothermic reaction shifts the equilibrium to favor the products. The changing temperature produces an actual change in the equilibrium constant. We can see the temperature dependence of the equilibrium constant in the following equation.

$$K = e^{\frac{-\Delta G^{\circ}}{RT}}$$
$$K = \left(e^{\frac{-\Delta H^{\circ}}{RT}}\right) \left(e^{\frac{\Delta S}{R}}\right)$$

Choice 'II' is not correct, however. Even though increasing the pressure will shift the reaction to favor the products, it will not change the actual value of the equilibrium constant. Changing the total pressure will affect the denominator of the reaction quotient, where there are more moles of gas, more than the numerator, so if the reaction had been at equilibrium, it would no longer be so, not because the actual equilibrium constant has changed but because the reaction quotient describing the state of the system will have changed and will no longer equal the equilibrium constant.

Choice 'III' is not correct, one of the oldest MCAT questions. A catalyst does not change the position of equilibrium. It will have no effect on the standard free energy change of the reaction. It will only affect the rate of the reaction.

5. B

The equilibrium constant, K_c , for a reaction is a particularly important value of the reaction quotient, Q_c . (The 'c' subscript here signifies that the equilibrium constant and reaction quotient are being expressed in terms of concentration rather than partial pressures, which is an issue for gaseous reactions.) There are many possible values of the reaction quotient, Q_{c} . You might have a lot of reagent and little product, or you might have a lot of product and a little reagent. Reaction quotient gives you a way to capture those different possible states of the system. If the reaction quotient is smaller than the equilibrium constant, it means that the reaction has a greater proportion of reagents than would be present at equilibrium, and the reaction will be spontaneous forward. If the reaction quotient is larger than the equilibrium constant, we have a higher proportion of products at present than the equilibrium state, and the reaction will be spontaneous in the reverse.

For our problem, we are told that 0.01 mol of each gas is present within the 1L reaction vessel, so the concentration of all three gases is 0.01M. From this we can compute the reaction quotient describing the current state of the system.

$$Q_{\rm c} = \frac{[{\rm SO}_3]^2}{[{\rm SO}_2]^2 [{\rm O}_2]}$$
$$Q_{\rm c} = \frac{(0.01 \,\text{M})^2}{(0.01 \,\text{M})^2 (0.01 \,\text{M})} = 100 \,\text{M}^{-1}$$

The reaction quotient is greater than the equilibrium constant, so the reverse direction is spontaneous.

6. C

The direction of spontaneity for a reaction doesn't only depend on the standard free energy change, ΔG° , which predicts the direction of spontaneity *if the concentrations of reagents and products are all 1M*. The direction of spontaneity also depends on the reaction quotient, Q.

$\Delta G = \Delta G^{\circ} + RT \ln Q$

Even with a negative standard free energy change, the reaction might be going in the reverse if the concentration of products is much greater than reagents.

7. C

The standard free energy change determines the equilibrium constant.

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

Likewise, you can determine the standard free energy change from the equilibrium constant.

$$\Delta G^{\circ} = -2.3 RT \log K$$

$$\Delta G^{\circ} = (-2.3)(8.3 \text{ J mol}^{-1} \text{ K}^{-1})(298\text{ K})(\log 1/9)$$

$$\sim (-2)(8)(300)(-1) \text{ J mol}^{-1}$$

$$\sim +5 \text{ kJ mol}^{-1}$$

8. A

A classic in chem 101, you are not likely to run into the full problem like this on the MCAT, where solution of a quadratic equation is necessary. If such a problem were to show up on the MCAT, simplifying assumptions would likely prevail, such as reagent consumed being very small compared to the starting concentration. Nevertheless, it's important to see a full example solved because it's an archetypal problem.

We begin with 1.0 mole of both carbon monoxide and water vapor in a 2 liter container (don't forget to dilute to 0.50 M). Equal in the stoichiometry, let's call the concentrations of carbon dioxide and hydrogen at equilibrium "x" and our remaining concentrations of carbon monoxide and water vapor each "0.50 - x".

$$K = \frac{[x][x]}{[0.5 - x][0.5 - x]} = 4.05$$
$$\frac{x^2}{0.25 - x + x^2} = 4$$
$$3x^2 - 4x + 1 = (3x - 1)(x - 1) = 0$$
$$x = 1 \text{ or } 0.33$$

We started with [CO] = 0.5 M, and we will lose 0.33 M, so our answer is 0.17 M.

9. B

Le Chatelier's principle tells us that if product is removed from a reaction vessel, the equilibrium shifts to make more product. Because the products here are gases in an open container, and these are continually dissipating into the surroundings, the reaction keeps moving forward trying to find the equilibrium state which it can never reach.

It is very common in biochemistry to see the product of a reaction in a biochemical pathway as the reagent for the next step. Forward flux is maintained by product removal.

10. A

You don't always need to be able to see all the way to the end of a problem to know how to get started. If you don't know where to begin, write some things down that you know and do your thinking on the page. Let the problem unfold.

Dalton's Law states that in a mixture of non-reacting gases, the total pressure exerted is equal to the sum of the partial pressures of the individual gases, so we can make the following statement about the pressures in the reaction vessel at equilibrium.

$$P_{NH3} + P_{CO2} = 0.117$$
 atm

We also know from the stoichiometry of the reaction: $P_{_{NH3}} = 2P_{_{CO2}}$

Combining these equations it is easy to show that:

$$P_{CO2} = 0.039 \text{ atm}$$

 $P_{NH3} = 0.078 \text{ atm}$

The solid reagent has a constant concentration, so it will not appear in K_{p} .

$$K_{\rm p} = (P_{\rm NH3})^2 (P_{\rm CO2}) = (7.8 \times 10^{-2})^2 (3.9 \times 10^{-2})$$

= 2.4 × 10⁻⁴

11. C

The forms of elemental sulfur described in the passage are molecular solids. A molecular solid consists of discrete molecules. The forces that bind the molecules together are intermolecular forces, ie. Van der Waals forces, dipole-dipole interactions or hydrogen bonds. For monoclinic and rhombic sulfur, the forces between S_8 molecules are Van der Waals forces. This is because S_8 molecules are nonpolar. The relatively high melting point for these crystals is because S_8 molecules are relatively large.

12. B

Each unit cell will share an S_8 molecule at each vertex with eight neighbors. There are eight vertices, so the unit cell will have eight atoms of sulfur total.

13. B

Notice that for each 10K increase in temperature, the enthalpy of rhombic sulfur increases 200 J. Therefore the molar heat capacity is 20 J mol⁻¹ K⁻¹. We were asked for the specific heat so we must convert to J g⁻¹ K⁻¹. The molecular weight of S_8 is 257 g/mol.

$$\left(\frac{20 \text{ J}}{\text{mol K}}\right) \left(\frac{1 \text{ mol}}{257 \text{ g}}\right) = \frac{.08 \text{ J}}{\text{g K}}$$

14. C

As the table data in the passage represents, the enthalpy of monoclinic sulfur at a given temperature is greater than the enthalpy of rhombic sulfur. The transformation of rhombic sulfur into monoclinic sulfur is endothermic. As temperature increases, equilibrium shifts to favor the endothermic direction of a reaction process. This is one of the most important applications of Le Chatelier's Principle. Choice 'I' is true.

Choice 'III' is also true. The standard free energy change is determined by both the enthalpy and the entropy. Being the higher entropy form, monoclinic sulfur is endowed with lower relative free energy at higher temperatures compared to rhombic sulfur.

15. A

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

In becoming liquid, both rhombic sulfur and monoclinic sulfur will be transformed into the same state (you can't tell from molten sulfur if it had been monoclinic or if it had been rhombic). Why would rhombic sulfur make the jump at a given temperature, but not monoclinic? The answer lies in their respective free energies. Rhombic sulfur possesses greater free energy at 113°C than monoclinic. Changing from rhombic to liquid represents a negative ΔG at 113°C, while to change from the lower free energy monoclinic sulfur at the temperature, the free energy change is positive, consistent with a non-spontaneous process, so monoclinic sulfur does not melt.

16. C

We must find a temperature where the free energy change from one allotrope to the other is zero.

$$\Delta G = \Delta H - T \Delta S = \mathbf{0}$$

Examining our table, we see that for all temperatures shown, the enthalpy and entropy changes involved in transforming one mole from rhombic to monoclinic sulfur are:

$$\Delta H_{\rm rh \, {\scriptstyle > \, \rm mc}} = 400 \, {\rm J}$$

$$\Delta S_{\rm rh \, {\scriptstyle > \, \rm mc}} = 1.1 \, {\rm J} \, {\rm K}^{\text{-1}}$$

Let's find the temperature where the free energy change is zero.

$$(400 \text{ J}) - T (1.1 \text{ J K}^{-1}) = 0$$

 $T = 364 \text{K}$

Chemical Kinetics Practice Items

- 1. Which of the following describes a first order reaction?
 - I. The reaction rate is directly proportional to the concentration of a single reagent.
 - II. Reagent concentration decreases with a half life that is independent of the initial reagent concentration.
 - III. A linear decrease of reagent concentration with time is observed.
 - A. I only
 - I and II **B**.
 - С. II and III
 - D. I, II, and III
- Which of the following is a homogeneous re-2. action?
 - $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O$ **A**.
 - **B.** $H_2O(g) \longrightarrow H_2O(l)$

 - C. $Ca(l) + H_2(g) \xrightarrow{\sim} CaH_2(s)$ D. $C(s) + H_2O(g) \xrightarrow{\sim} CO(g) + H_2(g)$
- 3. If the reaction rate is quadrupled by doubling the concentration of a reactant, the order of the reaction with respect to that reactant is
 - Α. 1
 - B. 2
 - **C**. 4
 - D. cannot be determined except by experiment

- In the presence of a catalyst 4.
 - I. Effective collisions among reactant molecules become more likely to occur.
 - II. Chemical equilibrium will shift toward the products.
 - III. The activation energy for the reaction is lowered.
 - **A.** I only
 - B. I and III
 - C. II and III
 - **D.** I, II, and III
- 5. Choose the correct rate expression for the reaction below

 $2MgO + Si \longrightarrow 2Mg + SiO_2$

- A. rate = k [MgO] [Si]
- rate = $k [MgO]^2 [Si]$ **B**.
- C. rate = 2k [MgO][Si]
- D. can't determine from given information
- 6. In general the rate constant is **not** a function of
 - **A**. the activation energy of the reaction.
 - B. reaction temperature.
 - concentration of reactants. **C**.
 - the probability of collision. D.
- H₂ and O₂ can be kept together at standard 7. conditions for many years without appreciable reaction to form water. The reaction doesn't occur because
 - equilibrium favors the reagents. Α.
 - the standard free energy change for the **B**. reaction is positive.
 - pressure in the reaction vessel is too С. low.
 - the mixture of gases is kinetically sta-D. ble.

Chemical Kinetics

8. The table below contains experimental data for the reaction

 $2A + 2B \longrightarrow C + 2D$

Trial #	Initial [A]	Initial [B]	Initial Formation Rate of C	
1	2.0 X 10 ⁻⁴ M	1.0 X 10 ⁻² <i>M</i>	8.0 X 10 ⁻⁵ <i>M sec</i> ⁻¹	
2	4.0 X 10 ⁻⁴ M	2.0 X 10 ⁻² <i>M</i>	6.4 X 10 ⁻⁴ <i>M sec</i> ⁻¹	
3	2.0 X 10 ⁻⁴ <i>M</i>	3.0 X 10 ⁻² <i>M</i>	2.4 X 10 ⁻⁴ <i>M sec</i> ⁻¹	

Which of the following is the correct rate equation for the reaction?

- **A.** rate = $k [A]^2 [B]^2$
- **B.** rate = k [A][B]
- **C.** rate = $k [A]^2 [B]$
- **D.** rate = $k [A]^2 [B]^3$

9. The decomposition of N_2O_5 in carbon tetrachloride can be represented

$$N_2O_5 \longrightarrow 4NO_2 + O_2$$

The reaction rate equation was found to be

rate = $(6.9 \times 10^{-4} \text{ s}^{-1}) [N_2 O_5]$

If we begin with 30 g of N_2O_5 in solution, approximately how much time elapses before only 1 g remains?

A.	$5.0 \times$	10^{3}	S
B.	$1.4 \times$	10^{4}	S

B.
$$1.4 \times 10^{4}$$
 s
C. 2.0×10^{4} s

D.
$$4.0 \times 10^4$$
 s

The following passage pertains to questions 10-12.

Reaction of an alkyl halide with base can proceed by either a substitution or an elimination pathway. The substitution that tert-butyl bromide would undergo with base is represented by the reaction below.

$$(CH_3)_3Br + OH^- \longrightarrow (CH_3)_3OH + Br$$

It has been found that the rate of the substitution reaction by which tert-butyl bromide is converted to tert-butyl alcohol varies directly with the concentration of alkyl halide but does not depend upon the concentration of base. The rate equation for the reaction is as follows:

rate =
$$k [(CH_3)_3Br]$$

Below is the energy diagram representing the reaction mechanism. The energy of the stages from A (reactants) to E (products) is shown.



- **10.** Which of the following best describes the reaction of tert-butyl bromide to form tert-butyl alcohol?
 - A. endothermic unimolecular
 - **B.** exothermic unimolecular
 - **C.** endothermic bimolecular
 - **D.** exothermic bimolecular

- **11.** The vertical difference on the graph between stages A and B represents
 - A. the enthalpy change of the reaction.
 - **B.** the activation energy of the reaction.
 - **C.** the enthalpy of the intermediate.
 - **D.** the enthalpy difference between the reagents and the reaction intermediate.
- **12.** Which of the following is the rate determining step in the reaction of tert-butyl bromide to form tert-butyl alcohol?
 - **A.** formation of the carbocation intermediate.
 - **B.** capture of the carbocation intermediate by hydroxide ion.
 - **C.** backside displacement of bromide by hydroxide ion.
 - **D.** direct displacement of bromide by hydroxide ion.
- **13.** The concentration of trimethylbromide changes with time during the reaction described in the passage according to the following equation.

 $\ln [(CH_{3})_{3}Br] = \ln [(CH_{3})_{3}Br]_{0} - kt$

Experimental data was plotted on the graph below. What is the approximate rate constant for the reaction?

- **A.** $4.0 \times 10^{-4} \text{ s}^{-1}$ **B.** $1.3 \times 10^{-3} \text{ s}^{-1}$
- C. $3.9 \times 10^{-3} \text{ s}^{-1}$
- **D.** $2.0 \times 10^{-2} \text{ s}^{-1}$



The following passage pertains to questions 14-17.

The Haber Process combines nitrogen from the air with hydrogen derived from methane to form ammonia. The reaction is reversible. The production of ammonia is exothermic.

$$N_2(g) + 3H_2(g) \implies 2NH_3(g)$$

$$\Delta H = -92 \text{ kJ mol}^{-1}$$

This conversion is typically conducted at 150-250 atm and between 300-550 °C, as the gases are passed over four beds of an iron wool catalyst, with cooling between each pass. The reaction mechanism involving the catalyst involves a number of steps of which the adsorption and cleavage of nitrogen is the rate determining step. Iron is predominantly in the zero oxidation state in the catalyst. Importantly, the rate-limiting step of the catalytic process is N2 chemisorption and N-N bond cleavage to give surface-bound nitrides (N^{3-}) , which react with H₂ to form the N-H bonds in NH₃. On each pass only about 15% conversion occurs, but any unreacted gases are recycled, and eventually an overall conversion of 97% is achieved.



Gaseous ammonia is not removed from the reactor itself, since the temperature is too high. It is removed from the equilibrium mixture of gases leaving the reaction vessel. The hot gases are cooled enough, whilst maintaining a high pressure, for the ammonia to condense and be removed as liquid. Unreacted hydrogen and nitrogen gases are then returned to the reaction vessel to undergo further reaction.

- **14.** Which of the following could we expect to increase the concentration of ammonia in the equilibrium mixture of gases exiting the reaction chamber?
 - I. Increasing pressure in the reactor.
 - II. Changes to the catalyst that lower the activation energy for the N_2 adsorption and cleavage steps.
 - III. Redesigning the reactor to accomodate a reaction temperature of 650 °C.
 - **A.** I only
 - **B.** I and III
 - C. II and III
 - **D.** I, II, and III
- **15.** The reaction is carried out at high temperatures in order to
 - A. decrease the equilibrium constant.
 - **B.** increase the equilibrium constant.
 - C. increase the rate constant.
 - **D.** decrease the activation energy.
- **16.** Why does the design call for the iron catalyst to be utilized in the form iron wool?
 - **A.** increased surface area
 - **B.** increased effective concentration
 - C. increased molar density
 - **D.** decreased heat capacity

- 17. It is believed that three iron atoms in the catalyst cooperate to break the N-N triple bond through a six-electron reduction of the N_2 . After the mechanism is complete and the ammonia is released, the iron will be
 - **A.** in the Fe_2N form of ferrous nitride.
 - **B.** in the $\overline{\text{Fe}_3N_4}$ form of ferrous nitride.
 - C. in the zero oxidation state of pure iron.
 - **D.** in the +3 ferric oxidation state.

Chemical Kinetics

Answers and Explanations

1. B

Choice 'I' is correct. The reaction rate is directly proportional to the concentration of a single reagent in a first order reaction.

$$rate = k [A]$$

Choice 'II' is correct. A first order reaction will have a half-life that is independent of the initial reagent concentration. The half-life is a function of the rate constant. The higher the rate constant the shorter the half-life.

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.69}{k}$$

Choice 'III' is incorrect. With a first order reaction, there is not a linear decrease of reagent concentration with time but an exponential decrease.

$$[A] = [A]_0 e^{-kt}$$

2. A

Homogeneous reactions are chemical reactions in which the reactants and products are in the same phase, while heterogeneous reactions have reactants in two or more phases. Reactions that take place on the surface of a catalyst of a different phase are also heterogeneous.

3. B

If the reaction rate quadruples in an experiment when the concentration of a reagent is doubled, the exponent for that reagent in the rate expression will be 2. The reaction is second order for that reagent.

4. B

Choices 'I' and 'III' are true. 'II' is not true. A catalyst speeds up both the forward and reverse reactions. A catalyst does not change the thermodynamics of the reaction, ie. the free energy change between products and reagents. A catalyst affects the kinetics.

5. D

The stoichiometry of a reaction will not reveal the rate expression. The stoichiometry does not reveal which species are present in the rate determine step of the reaction. You can determine a rate expression only by analyzing experimental data or if you know specific mechanistic details.

6. C

A rate constant relates changes in the concentration of reagents to changes in reaction rate. The rate constant is a function of a variety of determinants of reaction rate such as temperature and activation energy. The factors underlying the rate constant for a reaction appear in the Arrhenius equation.

$$k = A e^{\frac{-E_A}{RT}}$$

T is the absolute temperature (in kelvins). E_a is the activation energy for the reaction. *A* is the pre-exponential factor, a constant for each chemical reaction. *A* depends on how often molecules collide when all concentrations are 1 mol/L and on whether the molecules are properly oriented when they collide.

7. D

This is an example of a reaction which, though spontaneous, does not occur at an appreciable rate without a catalyst under standard conditions because the activation energy is very high. Though not *thermodynamically stable*, hydrogen and oxygen gas comprise a mixture which is *kinetically stable*. some form of the following:

rate =
$$k [A]^x [B]^y$$

We need to determine what the order of the reaction is with respect to the concentrations of each reagent. Notice that in between trials #1 and #3 (through which [A] is constant), the reaction rate triples when [B] is tripled. Therefore the reaction is first order with regard to [B]. Between trials #1 and #2, the concentrations of both species are doubled. We know now that doubling [B], doubles the rate. The actual rate, though, is eight times greater, ie. four times greater than the effect of doubling [B], so the reaction rate is second order with regard to [A], quadrupling when [A] is doubled.

rate =
$$k [A]^2 [B]$$

9. A

With first order reactions, we can express the time for the concentration of reactant to be halved.

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.69}{k}$$
$$t_{1/2} = \frac{6.9 \times 10^{-1}}{6.9 \times 10^{-4} \text{ s}^{-1}} = 1.0 \times 10^3 \text{ s}^{-1}$$

The half-life is 1.0×10^3 s. This gives us what we need to determine the approximate mount of time for the concentration to decrease to $\frac{1}{30}$ of its original value. Because $\frac{1}{30}$ is approximately $\frac{1}{32}$, the time required will be approximately five half lives for that amount of reagent to be remaining or 5.0 $\times 10^3$ s.

10. B

On the reaction coordinate we can see that the enthalpy of the products 'E' is lower than the enthalpy of the reagents 'A'. The enthalpy decreased. Heat flowed out. The reaction is exothermic.

Additionally, because the rate of the reaction only depends on the concentration of alkyl halide, the rate determining step is 'unimolecular'.

11. B

Stage 'B' represents the transition state on the way to the intermediate 'C' (the carbocation formed after the departure of the leaving group). The energy barrier to achieve the highest energy transition state in a reaction is the activation energy of the reaction. This is the rate determining step of the reaction.

12. A

The reaction described in the passage is SN1 substitution. The rate determining step is the departure of the leaving group, in this case, bromide, to form a carbocation. The carbocation will be subsequently captured by the nucleophilic hydroxide.

13. A

An important skill for the exam to be able to associate a formula in a linear form with a linear plot. First order kinetics represents a classic of this genre. In the given equation in slope-intercept form, the slope is -k.



We need to choose two points on the line to graphically determine the slope. The points (0,-1.25) and (5000,-3.25) look convenient.

$$-k = slope = \frac{rise}{run} = \frac{(-3.25 - -1.25)}{(5000s - 0s)}$$
$$= 4.0 \times 10^{-4} \, s^{-1}$$

14. A

'I' is correct. There are four moles of gas on the reagent side of the reaction and only two moles on the product side. Le Chatelier's principle teaches us that increasing the pressure for such a reaction at equilibrium will shift the equilibrium to favor the side of the reaction with a lower volume, ie. fewer moles of gas.

'II' is incorrect. Although improvements in the performance of the catalyst could definitely increase the *practical yield* of the reaction, the question is specific to the equilibrium yield of NH, in the gases leaving the reaction vessel as described in the passage. Across the entire span of general science, one of the most generative themes for the MCAT writers is the distinction between reasoning based on principles is of chemical thermodynamics and reasoning based on principles of chemical kinetics. One of the most common questions, often in the context of enzyme activity, turns on the understanding that a catalyst does not change the equilibrium constant of a reaction. The equilibrium constant depends on the standard free energy change of the reaction.

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

This is thermodynamics reasoning. It's about state functions. Free energy is a state function. Free energy is built out of the state functions of the system whose change affects the entropy of the whole universe. If the entropy of the universe increases, a process is spontaneous. Things are changing. Events move forward and the change to the universe isn't reversible. Everyone knows the formula G = H - TS. Free energy is a state function built out of the enthalpy, temperature and entropy of the system.

While we're on the topic, it's worthwhile to ask how does the free energy keep track of the entropy of the whole universe? These state functions of the system change, the enthalpy and entropy of the system, and this tells us something about the whole universe? How does that work? The universe is basically what we're calling the system plus everything else that's not the system. This other part of the universe that's not the system we refer to as the surroundings. Free energy keeps track of the entropy of the universe. We're keeping track of the entropy of the system plus the entropy of the surroundings. The entropy of the system is ΔS . The change in the entropy of the surroundings is $-\Delta H \div T$. The entropy of the surroundings is affected by the heat flow that occurs in the reaction. If the reaction moving in some direction increases the entropy of the universe through those two combined effects, the reaction will be moving towards some definite state that is different than the state it's currently in. It will move towards some equilibrium state. Free energy gives us a way to keep track of just how the movement towards equilibrium in a chemical reaction is increasing the entropy of the universe. That's the free energy change. That's how it works as a state function. Free energy is a state function of the system that when it changes means the entropy of the universe is changing.

That's thermodynamic thinking. It's about state functions. A change in a state function is *path independent*. The free energy change doesn't depend on the path between two states of the system. The two pillars of understanding that help you understand all chemical change are chemical thermodynamics and chemical kinetics. Chemical thermodynamics doesn't depend on the path while the kinetics of a reaction are path dependent.

In summary, why doesn't a catalyst affect the state of equilibrium? A catalyst doesn't affect the chemical thermodynamics. It only changes the path of the reaction. It affects the kinetics. The presence of a catalyst changes neither the initial nor the final state of a reaction process. A catalyst gives a reaction a different path from reactants to products and vice versa. It doesn't change the free energy comparison of any state of the system with any other state, nor does it have anything to do with what the equilibrium state of the reaction is. That's determined by the standard free energy change of the reaction which is independent of the activation energy of any particular reaction path. That's why choice 'II' is incorrect.

Choice 'III' is incorrect as well. The forward direction of the reaction is exothermic. ΔH is negative. Increasing the temperature shifts the position of equilibrium in favor of the endothermic direction of the reaction. This would decrease the equilibrium yield of the NH_3 in the gases leaving the reaction vessel.

15. C

The effect of temperature change on a rate constant can be seen in the Arrhenius equation.

$$k = A e^{\frac{-E_A}{RT}}$$

Increasing temperature increases the rate constant (leading to a smaller negative exponent in the equation). To see it more directly, think of the Maxwell-Boltzmann distribution of the reactant-product mixture. Increasing temperature increases the fraction in the vessel with sufficient energy to cross the activation energy barrier. The increase in the rate constant is reflected in an exponential increase in reaction rate with Kelvin temperature.

Regarding choice 'A'. Increasing temperature will lower the equilibrium constant. The choice is true in isolation, but to decrease the equilibrium constant is obviously not the reason the reaction is carried out at high temperature. That would lower the equilibrium yield. The reason for high temperature is to promote the kinetics and increase the practical yield of our reactor.

16. A

A reaction takes place on the surface of the solid iron catalyst and the nitrogen. Formation of the intermediate gives a path for the reaction. The surface area of a solid catalyst has a strong influence on the number of available active sites for catalyst-reagent intermediate to form. In industrial practice, solid catalysts are often porous to maximize surface area.

17. C

At the end of the reaction process, the catalyst must have returned to its initial state. Otherwise, it wouldn't be a catalyst. It would be a reagent appearing in the stoichiometry.

Solutions Practice Items

- **1.** Which of the following is a solution?
 - A. 14 carat gold
 - **B.** milk
 - C. foggy air
 - D. cytoplasm
- 2. The number of gram molecular weights of a solute per liter of solution is called the
 - A. molality
 - **B.** normality
 - **C.** formality
 - **D.** molarity
- **3.** How many grams of NaOH are required to prepare 250 ml of 2.0 *M* NaOH solution?
 - **A.** 5.0 g
 - **B.** 10.0 g
 - **C.** 17.5 g
 - **D.** 20.0 g
- 4. How much water must be added to 35.0 ml of 0.500 *M* NaOH solution to produce a solution whose concentration is 0.350 *M*?
 - **A.** 15.0 ml
 - **B.** 25.0 ml
 - **C.** 35.0 ml
 - **D.** 50.0 ml

- 5. A solution of silver nitrate is labeled 0.100 MAgNO₃. How many milliliters of this solution contain 8.50 g AgNO₃?
 - **A.** 0.1 L
 - **B.** 0.5 L
 - **C.** 2.0 L
 - **D.** 5.0 L
- 6. A solution is in equilibrium with another phase in which one of the solution components is in the form of a pure substance. Which of the following statements best describes the state of the system?
 - **A.** The solute has low solubility in this particular solvent.
 - **B.** The solution has precipitated.
 - **C.** The solution is saturated.
 - **D.** The solution process requires heat flow from the environment.
- 7. After dissolving ten grams of an unknown substance in 100ml deionized H_2O , the conductivity of the solution increased from 5.5 μ S/m to 7.2 S/m. The unknown substance is
 - A. an acid
 - **B.** a base
 - C. an electrolyte
 - **D.** a polar substance
- 8. Which of the following when dissolved in water would form hydrogen bonds with the water?
 - A. acetone
 - **B.** methanol
 - C. formaldehyde
 - **D.** all of the above

- **9.** 25g of lithium selenite, Li₂SeO₃, can dissolve in 100ml H₂0 at 5°C. At 95°C, only 10g will dissolve. From this information we may conclude:
 - A. lithium selinite is a weak electrolyte.
 - **B.** dissolving lithium selinite in water is an exothermic process.
 - **C.** lithium selinite is a strong electrolyte.
 - **D.** cooling a saturated Li_2SeO_3 solution produces a solution which is super-saturated.
- **10.** That the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid is a statement of:
 - A. Henry's law
 - **B.** Dalton's law
 - C. Raoult's law
 - **D.** Boyle's law
- **11.** Which statement follows from the graph below depicting the relationship between the solubility of substance A in aqueous solution and the temperature.
 - **A.** Substance A is an electrolyte.
 - **B.** Dissolving substance A at constant temperature causes heat to flow from the environment into the solution.
 - **C.** Dissolving substance A is more difficult at higher temperature.
 - **D.** Dissolving substance A decreases the boiling point of the solution.



- **12.** A quantity of lithium chloride sufficient to create a saturated solution at ambient temperature is added to water at that temperature and the mixture becomes warm. Which of the following is most likely to occur?
 - **A.** The solution is found to have an acidic pH on testing with litmus.
 - **B.** The solution is found to have a basic pH on testing with litmus.
 - C. Hydrogen gas evolves from the solution.
 - **D.** Not all the LiCl will dissolve until the solution returns to ambient temperature.
- 13. The freezing point depression constant K_f of water is 1.86 °C/m. When a 1 molal solution of KBr was tested, the freezing point depression was found to be 3.5°C because
 - A. In this solution, KBr creates 2 moles of ions per mole of solute dissolved.
 - **B.** The van't Hoff factor for KBr at this concentration and temperature is 2.
 - C. The degree of dissociation is 88%.
 - **D.** All of the above
- 14. Which of the following occurs when 0.5 liter 0.2 M CaCl₂ is combined with a 0.5 liter solution saturated with CaCO₃ ($K_{sp} = 4.9 \times 10^{-9}$)?
 - A. no precipitation
 - **B.** precipitation of $CaCO_3$
 - C. formation of supersaturated solution
 - **D.** precipitation of $CaCl_2$

- **15.** The K_{sp} of PbCO₃ = 7.4 × 10⁻¹⁴, while the K_{sp} of PbSO₄ is 2.0 × 10⁻⁸. If equal volumes of saturated solutions of the two salts were combined,
 - A. only lead carbonate would precipitate.
 - **B.** only lead sulfate would precipitate.
 - **C.** both lead sulfate and lead carbonate would precipitate.
 - **D.** neither salt would precipitate.
- 16. After a stream of air was bubbled through a 150g sample of diethyl ether $(C_4H_{10}O)$, the mass of the ether was found to have decreased by 10g. Subsequently, 9g of an unknown, nonvolatile substance was then dissolved in 150g of ether and a stream of air was bubbled through the solution under the same conditions as the prior experiment. After the process, the mass of the solution was found to have decreased by 9.5g. What is the approximate molecular weight of the unknown compound?
 - **A.** 35 g
 - **B.** 60 g
 - **C.** 90 g
 - **D.** 180 g
- **17.** After addition of excess HBr to a suspension of insoluble $CuCO_3$, the $CuCO_3$ dissolves and
 - A. the solution turns a bright color.
 - **B.** a bluish-grey precipitate forms.
 - C. a gas evolves.
 - **D.** chemiluminescence is observed.

The following passage pertains to questions 18 - 20.

A silver halide compound is one of the compounds formed between silver and one of the halogens silver bromide (AgBr), chloride (AgCl), iodide (AgI), and three forms of silver fluoride. Although most silver halides involve silver atoms with oxidation states of +1 (Ag⁺), silver halides in which the silver atoms have oxidation states of +2 (Ag²⁺) are known, of which silver(II) fluoride is the only known stable compound.

Silver halides, except for silver fluoride, are only very sparingly soluble in water. Silver nitrate can be used to precipitate halides. This application is useful in quantitative analysis of halides. However, close attention is necessary regarding other compounds in the test solution because some compounds can considerably increase or decrease the solubility of AgX. The solubility product constants of AgCl, AgBr, and AgI are, respectively, 1.7×10^{-10} , 4.1×10^{-13} , and 1.5×10^{-16} .

- **18.** If a solution containing concentrated KBr is stirred with solid AgCl
 - A. silver will be oxidized.
 - **B.** AgCl will dissolve and solid AgBr will precipitate.
 - **C.** no reaction will occur.
 - **D.** silver will be reduced.
- **19.** 100 ml 0.3 M AgNO₃ is combined with 50 ml of a sample taken from a larger volume solution to be tested for Br⁻. What is the detection limit for Br⁻ in the original sample by this method?

A. 2.0×10^{-12} M B. 6.0×10^{-12} M C. 1.2×10^{-11} M D. 1.4×10^{-10} M

Solutions

- **20.** Ammonia combines with silver ions to produce a complex ion called the diamminesilver(I) ion, $[Ag(NH_3)_2]^+$. This is a reversible reaction, but the complex is very stable. The addition of ammonia to a solution in contact with silver chloride precipitate will cause
 - A. silver chloride to dissolve.
 - **B.** nitrous oxide gas to be released.
 - C. ammonium chloride to precipitate.
 - **D.** silver chloride to precipitate.

The following passage pertains to questions 21 - 22.

An azeotrope is a mixture of two or more liquids in such a way that its components cannot be altered by simple distillation. This happens because, when an azeotrope is boiled, the vapor has the same proportions of constituents as the unboiled mixture.

There are two types of azeotropes called minimum boiling azeotrope and maximum boiling azeotrope. The solution which show a greater positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition. For example ethanol-water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution containing approximately 95% by volume of ethanol. Once this composition, has been achieved, the liquid and vapor have the same composition, and no further separation occurs. The figure below shows the phase diagram for water-ethanol mixture. The vertical axis is temperature. The horizontal axis is composition.



Solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass, with a boiling point of 393.5 K. The figure below shows the phase diagram for water-nitric acid mixture.



- **21.** The vapor pressure of an ethanol-water mixture
 - **A.** may be greater than the vapor pressure of 100% ethanol.
 - **B.** reflects a partial pressure ratio which is the same as the molar ratio in the liquid for all proportions of water and ethanol.
 - C. attains a minimum value at 95.4% ethanol.
 - **D.** is greater than the external pressure except at the azeotropic proportions of water and ethanol.
- **22.** Carrying out the fractional distillation of a 75% nitric acid solution
 - A. may converge on pure nitric acid.
 - **B.** may yield some pure water.
 - **C.** will only yield a 68% nitric acid solution.
 - **D.** produces a 90% nitric acid solution.

Solutions Answers and Explanations

1. A

A solution is a homogeneous mixture. Foggy air, milk, and cytoplasm are all heterogeneous. Within the mixture, at the molecular level, there are a variety of different phase spaces. Foggy air includes a suspended mist of water droplets. Both milk and cytoplasm are heterogeneous emulsions. They are colloidal suspensions. 14 carat gold, though, is a solution. It's a homogeneous alloy of gold, silver, copper and zinc. It is a true solution.

2. D

Molarity is the concentration of a solution expressed as the number of moles of solute per liter of solution, the concentration in terms of the spatial density of the molecules of solute. As such, molarity is the concentration expression that is directly proportional to the thermodynamic or kinetic activity of the solute, so we use molarity for equilibrium constants and rate expressions, for example.

3. D

Multiplying the concentration of a solution in molarity times the volume of a solution will give you the moles of solute in the solution (moles per liter times liters equals moles).

MV = moles of solute

(2.0 M)(0.25 L) = 0.5 mol NaOH

The molecular weight of NaOH is 40 g mol⁻¹.

 $(0.5 \text{ mol})(40 \text{ g mol}^{-1}) = 20 \text{g NaOH}$

4. A

When a solution is diluted, you know that the amount of solute stays the same. This proposition takes the form of the *dilution equation*, which is basically that the product of the molarity and volume will be constant given that the amount of solute isn't changing.

$$M_1 V_1 = M_2 V_2$$

(0.5 M)(0.035L) = (0.35 M) V_2
 $V = 0.05$ L

So we need to add 15ml in order to increase the volume from 35ml to 50ml.

5. B

The molecular weight of $AgNO_3$ is 170 g/mol. Just as molecular weight allows you to convert moles to grams, the reciprocal of the molecular weight is the conversion factor to convert grams to moles.

8.5 g AgNO₃
$$\frac{1 \text{ mol AgNO}_3}{170 \text{ g AgNO}_3} = 0.05 \text{ mol AgNO}_3$$

That makes it easier. How many milliliters of 0.1M AgNO₃ solution contain 0.05 mol AgNO₃?

MV = moles of solute(0.1 M) $V = 0.05 \text{ mol AgNO}_3$ V = 0.5 L

6. C

Of all the choices, only choice 'C' is definitely true. A saturated solution is at equilibrium. The rate of dissolution and the rate of reforming the solid solute are equal. The other choices *may* be true.

7. C

An electrolyte is a substance that produces an electrically conducting solution when dissolved in a polar solvent, such as water. The dissolved electrolyte separates into cations and anions, which disperse uniformly through the solvent. Many Brønsted acids are electrolytes. Water itself is an electrolyte, which explains the conductivity of pure deionized water, the prototypical electrolyte is a salt. A salt solution conducts electricity through the movement of ions.

8. D

With methanol it's easy to see. A hydroxyl group is great at hydrogen bonding, so methanol with hydrogen bond with the water. With acetone and formaldehyde, it's a little harder to see at first, but they also will hydrogen bond with the water. This is true even though the type of intermolecular force which you will see prevailing in pure acetone or pure formaldehyde is dipole-dipole interaction. There is no hydrogen bonding in the pure forms of those substances because there are no functional groups in which a hydrogen is bound to a very electronegative element such as hydroxyl or amine groups.



However, in aqueous solution, the carbonyl oxygen will act as a *hydrogen bond receiver*.



9. B

One of the correlatives of Le Chatelier's Principle is that increasing temperature will shift an equilibrium to favor the endothermic direction. If a solution process were endothermic, solubility would *increase* with increasing temperature. In the case of lithium selenite, however, solubility decreases with increasing temperature. This means that the endothermic direction isn't the solution process but precipitation. Therefore, the solution process must be exothermic. This is an old favorite. If solubility does down with temperature, the solution process is exothermic.

10. A

Henry's Law has the mathematical form:

$$C_{g} = k P_{g}$$

11. B

One of the most important correlatives of Le Chatelier's principle is that increasing temperature shifts an equilibrium to favor the endothermic direction of a chemical process. Therefore, if solubility increases with temperature, we can conclude that the process of dissolving the particular solvent in that particular solvent is endothermic.

12. D

The solution became warm. This tells us that dissolving LiCl in water is an exothermic process. If the solution process is exothermic, solubility decreases when the temperature increases. According to Le Chatelier's principle, increased temperature favors the endothermic direction of a reaction process, which in this case would be precipitation. If the amount of solute added would saturate the solution at ambient temperature, this is more than the solvent can accommodate now that the temperature is elevated. It will take patience, allowing the solution to cool, to dissolve the LiCl.

13. C

Freezing-point depression is the decrease of the freezing point of a solvent that occurs on the addition of a non-volatile solute. The change in the freezing point is given by the following formula:

$$\Delta T_{\rm F} = K_{\rm F} \cdot m \cdot i$$

 $\Delta T_{\rm F}$, the freezing-point depression, is defined as $T_{\rm F}$ (pure solvent) – $T_{\rm F}$ (solution).

 $K_{\rm F}$, the cryoscopic constant, is dependent on the properties of the solvent, not the solute. For water, $K_{\rm F} = 1.853$ K·kg/mol.

m is the molality (moles solute per kilogram of solvent).

i is the van 't Hoff factor.

For the MCAT, when you're dealing with the dissociation of a strong electrolyte, it's not a bad working assumption to assume complete dissocia-

tion and just say i = 2. Each mole dissolved yields two moles of particles in the solution. For MgBr₂ we would say i = 3.

There is an ideal case where the van't Hoff factor is equal to the number of discrete ions in a formula unit of the substance, but in a more concentrated solution, especially, the van't Hoff factor can deviate. Occasionally ion pairing occurs in solution in real solutions. At a given instant a small percentage of the ions are paired and count as a single particle. This causes the measured van 't Hoff factor to be less than that predicted in an ideal solution.

If the van't Hoff factor were actually 2 here, the freezing point depression would be 3.72° C instead of 3.5° C. This is because the *degree of dissociation*, α , is less than 100%. If *n* equals the ideal van't Hoff factor, 2, then the actual van't Hoff factor can be determined from degree of dissociation:

$$i = 1 + \alpha(n - 1)$$

We don't need to do math to confirm the degree of dissociation is 88% because choices 'A' and 'B' are both saying the same thing inconsistent with the observed freezing point depression of 3.5°C.

14. B

While it should be apparent by inspection that combining a concentrated $CaCl_2$ solution with a saturated solution of $CaCO_3$ will lead to precipitation of $CaCO_3$, it's a good exercise to do the math. In the saturated solution of $CaCO_3$, the concentrations of the two ions are equal. In the saturated solution, each concentration equals the square root of K_{sp} .

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 4.9 \times 10^{-9}$$

 $x^2 = 49 \times 10^{-10}$
 $[Ca^{2+}] = [CO_3^{2-}] = 7.0 \times 10^{-5} M$

If we combine 0.5 L of this CaCO₃ solution with a 0.5 L solution of 0.2 M CaCl₂, we will have 1.0 L solution that is 3.5×10^{-5} M for CO₃⁻² and 0.1M

for Ca⁺². Note, firstly, that in combining the two 0.5L solutions we doubled the volume, which halved the concentrations from the contributing solutions. Secondly, because the 0.1M Ca⁺² from the CaCl₂ is so much greater than the 3.5×10^{-5} M Ca⁺² from the CaCO₃ solution, we can ignore this contribution and treat the concentration after admixture as 0.1M. In summary, we have a solution with 0.1M Ca⁺² and 3.5×10^{-5} M CO₃⁻². Therefore, we have the following ion product.

$$Q_{\rm sp} = [{\rm Ca}^{2+}][{\rm CO}_3^{2-}] = 3.5 \times 10^{-6}$$

This is greater than the solubility product.

$$K_{sp} = [Ca^{2+}][CO_3^{2-}] = 4.9 \times 10^{-9}$$

If the ion product, $Q_{\rm sp}$, is greater than the solubility product, $K_{\rm sp}$, there are more ions in the solution than the equilibrium, saturated state. It will precipitate.

15. A

The solubility product, K_{sp} , is a simplified equilibrium constant representing the equilibrium state of a salt solution, the saturated solution. In other words, the product of the ion concentrations of a saturated solution equals K_{sp} . If the ion product is less than K_{sp} , more could dissolve. If the ion product is uct is greater than K_{sp} , the solution is precipitating.

$$[Pb^{2+}][CO_3^{2-}] = 7.4 \times 10^{-14}$$
$$[Pb^{2+}][SO_4^{2-}] = 2.0 \times 10^{-8}$$

In saturated PbCO₃ solution, the concentration $[Pb^{2+}]$ equals $[CO_3^{2-}]$. This is because when PbCO₃ dissolves, the ions dissociate in 1:1 stoichiometric ratio. Additionally, each of these concentrations equals the square root of 7.4×10^{-14} .

Analogous statements are true for the saturated $PbSO_4$ solution. In this solution, the respective $[Pb^{2+}]$ and $[SO_4^{2-}]$ concentrations equal the square root of 2.0×10^{-8} .

The concentrations of ions in the PbCO₃ solution are on the order of 10^{-7} M. The concentrations of ions in the PbSO₄ solution are on the order of 10^{-4}

M. If we combine the two solutions in equal mixture, the ion concentrations will be halved. Without the need for arithmetic, it's easy to see that in the final, combined solution, the ion product of PbSO₄ will be below its K_{sp} , but the ion product of PbCO₃ will be above its K_{sp} . This is because the carbonate ions now find themselves in a solution with lead ions on the order of 10⁻⁴ M. This will put the ion product of PbCO₃ on the order of 10⁻¹¹, so it is going to precipitate.

16. C

The basic conceptual vocabulary in physics and chemistry really isn't that large. Ttranslate the real world scenario presented into the simpler language of fundamental relationships. Bubbling the air through the ether resulted in a loss of mass of the solution 95% of the loss when bubbling the air through the pure ether. Dissolving the solute in the ether *decreased its vapor pressure* to 95% of its original value. From Rault's Law, we know that the mole fraction of ether in the second experiment is 95% of the original value. The vapor pressure of the solvent in the solution is proportional to the mole fraction of solvent.

$$P_{\rm A} = X_{\rm A} P_{\rm A}^{0}$$

 $P_{\rm A}^{0}$ is the vapor pressure of the pure solvent. $X_{\rm A}$ is the mole fraction of solvent in the solution. $P_{\rm A}^{0}$ is the vapor pressure of the solution.

We can conclude that the mole fraction of ether in the solution is 95%. The spacing of the answers is an invitation to use mental math. 150g of diethyl ether is 2 moles (MW = 74 g mol⁻¹). If this amount of ether represents 95% of the moles of the solution, then our added substance represents approximately 0.1 mol, one twentieth of 2 moles. If 9g represents 0.1 mole, its molecular weight must be approximately 90g.

17. C

Lowering the pH will increase the solubility of an insoluble or sparingly soluble electrolyte, such as copper(II) carbonate, whose anion is the conjugate base of a weak acid. The shifting acid base equilibrium to accommodate the lower pH will promote the solution process by removing the anion from the solution.

$$CuCO_{3} \rightleftharpoons Cu^{2+} + CO_{3}^{2-}$$
$$CO_{3}^{2-} + H^{+} \rightleftharpoons HCO_{3}^{-}$$
$$HCO_{3}^{-} + H^{+} \rightleftharpoons H_{2}CO_{3}$$

Additionally, a process leading to formation of excess carbon dioxide will be a gas evolution reaction. Carbonic acid decomposes forming carbon dioxide and water. Because of its importance in physiology, this is one of the MCAT's very favorite chemical reactions.

$$H_2CO_3(aq) \rightleftharpoons CO_2(g) + H_2O$$

18. B

When the solid AgCl is introduced to the solution, Ag⁺ and Cl⁻ ions will start dissociating and entering the aqueous phase. This solution process will be driving towards the K_{sp} of AgCl, but it won't be permitted to reach it, because long before the ion products reaches that value, the ion product of Ag⁺ and Br⁻ will cross the threshold of the K_{sp} of AgBr. Not only is the K_{sp} of AgBr lower than that of AgCl (it's less soluble), but the solution is concentrated for Br⁻. AgBr starts to precipitate. The precipitation of AgBr will couple with dissolution of AgCl until all of the AgCl has dissolved.

$$AgCl \rightleftharpoons Ag^{+} + Cl^{-}$$
$$Ag^{+} + Br^{-} \rightleftharpoons AgBr$$

19. B

To solve this problem, first we will need to determine the concentration of Ag⁺ in the combined solution after admixture. We will then use this Ag⁺ concentration along with the K_{sp} of AgBr given in the passage to determine the concentration of Br⁻ great enough to lead to precipitation.

Firstly, to determine the concentration of Ag^+ in the combined solution, we divide the moles of Ag^+ (concentration of the 1st solution times its volume) by the new combined solution volume.

The dilution is not hard to compute in your head, but it's good to see it worked it out to be ready for dilutions that may be a little more complicated.

$$\frac{(0.1L)(0.3 \text{ mol } L^{-1} \text{ Ag}^{+})}{(0.1L + 0.05L)} = \frac{3 \times 10^{-2} \text{ mol}}{1.5 \times 10^{-1} \text{ L}} = 2 \times 10^{-1} \text{ M}$$

Now we can use K_{sp} to determine the minimum concentration of Br⁻ to observe precipitation.

$$K_{\rm sp} = (2.0 \times 10^{-1})[{\rm Br}^{-}] = 4.1 \times 10^{-13}$$

 $[{\rm Br}^{-}] = 2.0 \times 10^{-12} {\rm M}$

We have found the minimum concentration of Br⁻ in the combined solution to observe precipitation. However, this concentration doesn't represent the detection limit. That detection limit is the concentration of Br⁻ in the original 50ml sample which corresponds to this. Although you might see that the original threshold concentration would have been three times greater, having diluted from 50ml to 150ml.

 $\frac{(0.05L)(original \ concentration)}{(0.1L + 0.05L)} = 2.0 \times 10^{-12} \text{ M}$

original concentration =
$$6.0 \times 10^{-12}$$
 M

This is the threshold concentration in the original 50ml sample for precipitation after admixture.

20. A

 $[Ag(NH_3)_2]^+$ is a complex ion. It has a metal ion at its center with a number of other molecules or ions surrounding it, attached via coordinate covalent bonds. The solution process for a weak electrolyte may be coupled with formation of a complex ion.

$$AgCl \rightleftharpoons Ag^{+} + Cl^{-}$$
$$Ag^{+} + 2NH_{3} \rightleftharpoons [Ag(NH_{3})_{3}]^{-}$$

The question stem indicated that diamminesilver(I) ion is very stable, so the equilibrium of complex ion formation will lie to the right. This will remove silver ions from the solution, driving the dissolution of AgCl forward by mass action.

21. A

At at 95.4% ethanol, the ethanol-water mixture has a boiling point of 78.15°C. This is lower than the boiling point of 81.3°C for pure ethanol. The standard boiling point describes the temperature at which the vapor pressure of a liquid comes to equal 1 atm. For the mixture to have a lower boiling point than pure ethanol, it must have a higher vapor pressure.

22. A

These types of phase diagrams depicting minimum and maximum boiling azeotropes are Chem 101 classics, so it's good to know your way around them. The diagrams show how the composition of the vapor coming off the liquid at a given temperature may differ from the composition of the liquid itself. Notice first leftward arrow in the diagram below. The vapor of a 75% nitric acid solution has more nitric acid than the liquid itself. When we condense that liquid, the downward arrow, the liquid is enriched for nitric acid. The process can continue with another round, which will yield even greater enrichment for nitric acid.



Notice that for a 75% nitric acid solution, being on the left side of the maximum boiling azeotrope, we would be unable produce pure water by fractional distillation.

Acids & Bases Practice Items

- 1. Which of the following could not act as a Lewis base?
 - A. NH_3
 - **B.** H[−]
 - C. CaO
 - **D.** CH₄
- 2. Which below is the weakest acid?
 - A. carbonic acid, H_2CO_3 ($K_a = 4.5 \times 10^{-7}$)
 - **B.** acetic acid, $CH_3CO_2H(K_a = 1.8 \times 10^{-5})$
 - C. phenol, $C_6H_5OH(K_a = 1.3 \times 10^{-10})$
 - **D.** boric acid, H_3BO_3 ($K_a = 5.8 \times 10^{-10}$)
- 3. Which of the following is the best explanation for why perchloric acid, $HClO_4$, is more acidic than hypochlorous acid, HOCl?
 - **A.** Chlorine is less highly oxidized in $HClO_4$ than in HOCl.
 - **B.** ClO_4^- is stabilized by charge delocalization.
 - C. Perchlorate is a strong nucleophile.
 - **D.** Hypochlorite is a weaker base than perchlorate.
- 4. What is pK_a of hypochlorous acid, HClO? ($K_a = 3.2 \times 10^{-8}$)
 - **A.** -2.4
 - **B.** 2.4
 - **C.** 7.5
 - **D.** 8.5

5. At 25°C the autoprotolysis of pure water, shown below, attains equilibrium hydronium and hydroxide ion concentrations of about 1 $\times 10^{-7}$ moles per liter, respectively. The equilibrium concentrations vary somewhat with temperature, however. At 0°C, the concentrations are about 8 $\times 10^{-8}$ moles per liter, and at 100°C the concentrations are about 7 $\times 10^{-7}$ moles per liter. What can we conclude about the autoprotolysis of water?

 $2H_2O$ \longrightarrow $H_3O^+ + OH^-$

- **A.** Autoprotolysis of water is a second order reaction.
- **B.** Autoprotolysis of water is an endothermic process.
- C. Autoprotolysis of water is spontaneous.
- **D.** Water is a strong electrolyte.
- 6. What is the approximate pH of the solution that results when 55 g of hydrocyanic acid, HCN, $(K_a = 4.9 \times 10^{-10})$ is dissolved in 20 liters of water?
 - **A.** 0.7
 - **B.** 3.5
 - **C.** 5.3
 - **D.** 6.5
- 7. When water is added to 1.0 g of an unknown diprotic strong acid to form 2 liter of solution, the pH of the resulting solution is 1.0. What is the molecular weight of the acid?
 - **A.** 10 g mol⁻¹
 - **B.** 20 g mol⁻¹
 - **C.** 100 g mol⁻¹
 - **D.** 200 g mol⁻¹

- **8.** What is the hydrogen ion concentration of a solution with a pOH of 3.5?
 - **A.** 3.2×10^{-11} M **B.** 5.0×10^{-10} M
 - C. $1.5 \times 10^{-10} \text{ M}$ D. $3.2 \times 10^{-4} \text{ M}$
 - **D.** 3.2×10^{-1} M
- **9.** In the laboratory, it was found that 50 ml of a solution containing an unknown amount of NaOH was neutralized by 200 ml solution containing an unknown amount HCl. The solution was then evaporated. The mass of NaCl recovered after evaporation was 5.9 g. What was the normality of the alkaline solution prior to mixture?
 - **A.** 0.5 N
 - **B.** 1.0 N
 - **C.** 2.0 N
 - **D.** 5.0 N
- **10.** If 0.5 liters of 4 N ammonium hydroxide is added dropwise to 2.0 liters of 1 N hydro-chloric acid, the resulting solution will be
 - A. weakly acidic
 - **B.** strongly basic
 - C. neutral
 - **D.** weakly basic
- **11.** Of the choices of common indicators listed along with the pH associated with their color changes, which would be most useful for determining the equivalence point in a titration of 1 N HNO₃ with 5 N NaOH?
 - A. methyl red (p K_a 4.95)
 - **B.** p-Nitrophenol $(pK_{a}, 7.2)$
 - **C.** thymol blue $(pK_a 8.9)$
 - **D.** allizarin yellow $(pK_a 11.2)$

- 12. Determine the pH of a of a 1 liter solution containing 1 mole of H_2CO_3 ($K_a = 4.5 \times 10^{-7}$) and 0.1 mol of NaHCO₃.
 - **A.** 3.5
 - **B.** 5.4
 - **C.** 6.8
 - **D.** 7.3
- **13.** Which results from combining excess concentrated HCl with concentrated K_2CO_3 ?
 - **A.** formation of a colored complex
 - B. precipitation
 - C. liberation of gas
 - **D.** a solution of weak base
- **14.** All of the following substances increase the concentration of hydronium ion in aqueous solution except
 - A. carbon dioxide
 - **B.** sulfur dioxide
 - C. phosphorus pentoxide
 - **D.** calcium oxide
- 15. Which of the following is the weakest acid?
 - A. HF
 - B. HCl
 - C. HBr
 - D. HI

- **16.** Which of the following is the strongest acid?
 - **A.** hypochlorous acid $H \ddot{O} \ddot{C}I$:
 - **B.** chlorous acid $H \ddot{O} \ddot{C}l = \ddot{O}$
 - **C.** chloric acid $H \ddot{\Box} \ddot{C}I = \dddot{O}$ \vdots **D.** perchloric acid $H - \ddot{\Box} - \ddot{C}I = \ddot{\Box}$
- 17. The side chain of the amino acid lysine has a pK_a of 10.5. Approximately what percent of lysine is not protonated at physiological pH?
 - **A.** 0.001%
 - **B.** 0.01%
 - **C.** 0.1%
 - **D.** 1.0%
- 18. The conformation of folded deoxyhemoglobin is such that a particular histidine residue on each α chain finds itself in close proximity to a particular aspartate residue which is distant on the primary structure. A salt bridge forms stabilizing both residues. Which of the following describes an effect of this association?
 - **A.** The pK_a of the histidine increases and that of aspartate decreases.
 - **B.** The pK_a of the histidine decreases and that of aspartate increases.
 - **C.** The pK_a of both residues increases.
 - **D.** The pK_a of both residues decreases.

19. The graph below shows the variation is pH as a weak acid is titrated with a strong base. What is the approximate pK_a of the acid?



- **20.** Which of the following substitutions would be expected to produced the greatest decrease in the isoelectric point of a globular protein?
 - **A.** A123D
 - **B.** F257R
 - **C.** K299E
 - **D.** F355Y

Acids & Bases Answers and Explanations

1. A

Within the subject of acids and bases, we will most often be situated within the Brønsted-Lowry system, where acid base activity is conceived in terms of proton exchange. However, the Lewis system is a useful conceptual framework. A Lewis base is any substance that can donate a pair of nonbonding electrons. A Lewis base is an electron-pair donor. Of the answer choices, all of them possess a nonbonded pair of electrons except for methane.

2. C

 $K_{\rm a}$ increases with increasing dissociation of the acid. Therefore, the smaller $K_{\rm a}$ the weaker the acid.

$$HA \rightleftharpoons A^- + H^+$$
$$K_a = \frac{[A^-] [H^+]}{[HA]}$$

3. B

When you ask about the strength of an acid you are asking about is the position of this equilibrium.

$$HA \rightleftharpoons A^- + H^+$$

The stronger the acid, the further to the right the position of this equilibrium. Remember that the position of an equilibrium is determined by the standard free energy change.

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

For strong acids, like perchloric acid, the standard free energy change is negative. For a weak acid like hypochlorous acid ($K_a = 3.2 \times 10^{-8}$), the standard free energy change is positive.

In summary, the question of why an acid is strong is really the question of why the standard free energy change of dissociation is negative. The answer can often be found in the stability of the conjugate base. For perchloric acid, the answer is that the conjugate base, perchlorate, is extremely resonance stabilized. Below are its four most prominent resonance forms.



The acidity of the many oxygen acids of nonmetals can be understood in terms of the resonance stabilization of the conjugate base, ie. sulfuric acid, phosphoric acid, carbonic acid, etc.

4. C

Just as with pH, pK_a is basically a way to write a number more conveniently. It converts a number in scientific notation with a negative exponent into a much simpler form. It goes back to a time when scientific notation was a big typographical hassle, but then the system then took on a life of its own, and it has become a valuable way to conceptualize things.

$$pK_a = -\log K_a$$

To understand how to take the pK_a of a number, firstly, remember the following about logarithms.

$$\log (ab) = \log (a) + \log (b)$$

So our problem becomes

$$pK_{a} = -\log (3.2 \times 10^{-8}) = -[\log (3.2) + \log (10^{-8})]$$

$$pK_{a} = -[\log (3.2) - 8]$$

$$pK_{a} = 8 - \log (3.2)$$

At this stage, for log(3.2) you might ask yourself 'to what power do I raise the number 10 to get 3.2?' This is near to the square root of 10, so $\frac{1}{2}$ then. Or you might use the linear interpolation shortcut and say log (3.2) ~ 0.32. For the MCAT, that's usually the way. Make the negative exponent a positive whole number and subtract $\frac{1}{10}$ of the coefficient from this whole number.

$$pK_{a} = -\log(3.2 \times 10^{-8}) \sim 8 - 0.3 \sim 7.7$$

6. C

To determine the approximate pH of our solution at equilibrium, we will start with the expression describing that equilibrium state, the K_a of HCN.

$$\frac{[\text{A}^{-}] [\text{H}^{+}]}{[\text{HA}]} = K_{\text{a}}$$

$$\frac{[\text{CN}^{-}] [\text{H}^{+}]}{[\text{HCN}]} = 4.9 \times 10^{-10}$$

There is a longer, more exact way to do this, and there is a shorter, more approximate way. The longer way takes into account the H⁺ ions already present in pure water, and it also assumes that the amount of the weak acid which dissociates is significant compared to the concentration of undissociated weak acid. This longer way involves a number of steps which will lead ultimately to the quadratic equation. All quantitative MCAT questions are designed to be solved more quickly than this. If you are asked to do this classic Chem 101 problem on the MCAT, the question stem will almost certainly say 'approximate pH' letting you know you have permission to use the shorter method.

For the shorter method, we make two assumptions. When the acid dissociates, for each mole of protons liberated, so also is a mole of conjugate base.

$$HA \rightleftharpoons A^- + H^+$$

Ignoring the already 10⁻⁷ M H⁺ in the water before admixture, our first assumption is as follows.

$$[\mathrm{H}^+] \approx [\mathrm{A}^-]$$

Additionally, we are going to assume that the concentration of acid which dissociates is very small compared to the initial concentration added.

$$[\text{HA}]_{\text{equilibrium}} \approx [\text{HA}]_{0}$$

In our problem we added approximately two moles of HCN (MW = 27g mol⁻¹) to 20L water making approximately 20L solution, so our initial concentration, $[HA]_0 \sim 0.1M$.

Now we can restate our expression for K_{a} using our approximations.

$$\frac{[\text{CN}^{-1}] [\text{H}^{+1}]}{[\text{HCN}]} = 4.9 \times 10^{-10}$$
$$\frac{[\text{H}^{+1}]^2}{0.1 \text{ M}} = 4.9 \times 10^{-10}$$
$$\frac{[\text{H}^{+1}]^2}{1 \times 10^{-1} \text{ M}} = 4.9 \times 10^{-10}$$
$$[\text{H}^{+1}]^2 = 4.9 \times 10^{-11}$$

To take the square root of a number in scientific notation, you need the exponent to be an even number.

$$[H^+]^2 = 49 \times 10^{-12}$$
$$[H^+] = 7 \times 10^{-6}$$

Now use your method for approximating pH when given $[H^+]$ in scientific notation. Make the negative exponent a positive whole number and subtract $\frac{1}{10}$ of the coefficient from this whole number.

$$pH = -\log(7 \times 10^{-6}) \sim 6 - 0.7 \sim 5.3$$

7. C

With this kind of problem, it's natural not to see the whole problem solving algorithm from start to finish in your head. Start working with what you know. Think with your pencil, and let the problem unfold. A big part of the art of this kind of thing is learning to trust yourself to just get started. We can see it's useful to convert the pH of the solution into hydrogen ion concentration, so let's do that.

$$pH = 1$$

$$-\log[H^{+}] = 1$$

$$[H^+] = 10^-$$

Now we can start rolling out conversion factors. Lay it out stepwise and work towards your goal.

We can multiply the volume of the solution times the H^+ concentration. This would give us the number of moles of H^+ in the solution.

(2 L)
$$\frac{(1 \times 10^{-1} \text{ mole H}^{+})}{L}$$

We were told it is a diprotic strong acid. This gives us a stoichiometric ratio to convert our moles of H^+ into moles of our acid.

 $(2 L) \frac{(1 \times 10^{-1} \text{ mole } H^{+})}{L} \frac{(1 \text{ mole acid})}{(2 \text{ mol } H^{+})} = 10^{-1} \text{ mole acid}$

So now we know that our 10g of acid equals 0.1 mole, so we can determine the molecular weight.

$$\frac{10g}{0.1 \text{ mol}} = 100 \frac{g}{\text{mol}}$$

8. A

To find $[H^+]$ we can begin by determining the pH, given that pOH = 3.5.

$$pH + pOH = 14$$
$$pH = 10.5$$
$$-log[H^+] = 10.5$$
$$log[H^+] = -10.5$$
$$[H^+] = 10^{-10.5}$$
$$[H^+] = (10^{0.5})(10^{-11})$$
$$[H^+] = 3.2 \times 10^{-11} M$$

Though the mathematical operations to move from pH to $[H^+]$ are useful to see, once it's determined that the pH is 10.5, it's possible to solve the problem by inspecting the answers because there's only once choice with $[H^+]$ between 10^{-11} and 10^{-10} .

9. C

Titration of an Arrhenius acid with an Arrhenius base produces a salt and water.

The titration described in the question stem yielded 5.9g NaCl (MW 59g). 5.9g equals 0.1 mol.

$$5.9 \text{ g} \frac{1 \text{ mol}}{59 \text{ g}} = 0.1 \text{ mol}$$

From the stoichiometric ratio in the titration reaction, it can be seen that if 0.1 mol NaCl was produced, 0.1 mol NaOH was consumed. Therefore the initial concentration was 2.0M.

$$\frac{0.1 \text{ mol}}{0.05 \text{ L}} = 2.0 \text{ M}$$

Because one mole of NaOH produces one mole of OH⁻, one mole represents one equivalent in titration. In other words, a 2.0M solution of NaOH is also 2.0N.

10. A

The equivalence point in a titration of acid with base is reached when you have added exactly as many equivalents of base as acid. This titration has reached the equivalency point.

$$N_{\text{acid}}V_{\text{acid}} = N_{\text{base}}V_{\text{base}}$$

(1 N)(2 L) = (0.5 L)(4 N)

Just because you have reached the equivalency point in a titration of an acid with a base does not mean the pH in the solution is neutral. You have to ask yourself what is actually in the beaker. In this case, we are titrating a strong acid with a strong base.

$$HCl + NH_4OH \rightarrow NH_4Cl + H_2O$$

Normally, one would expect the titration of a strong acid with a strong base to yield a neutral solution at equivalency, but the salt forming in this case is ammonium chloride, which is a weak acid.

11. B

At equivalency this titration will yield a solution of sodium nitrate. A sodium nitrate solution has a neutral pH.

$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$$

A pH indicator is a weak acid – weak base pair (HI and I⁻) where each of these is a different color. To interpret the behavior of an indicator when its color change occurs, it's helpful to see it within the framework of the Henderson-Hasselbalch equation.

$$pH = pK_a + \log\left(\frac{[I^-]}{[HI]}\right)$$

Using the Henderson-Hasselbalch equation in the context of a buffer solution, we see the ratio of the weak acid : weak base concentrations as the independent variable determining the pH of the solution. In the case of an indicator, however, we flip the script and think of the pH controlling the ratio of [I⁻] and [HI] instead of vice versa. (This is also how you should think of the state of ion-ization of biomolecules. Physiological pH dictates that an aspartate side chain is a reliable negative, for example.)

To choose an indicator, you want its pK_a to be as close to the pH of the equivalency point as possible. When the pH of the solution is a full unit below the pK_a of the indicator, the [HI]:[I⁻] ratio will be 10:1 and the solution will be one color. When the pH of the solution is a full unit above the pK_a of the indicator, the [HI]:[I⁻] ratio will be 1:10 and the solution will be a different color. If pK_a of the indicator is near to the pH of the equivalency point, this color change will occur as the pH sweeps across the equivalency point.

Because the equivalency point in our titration is a sodium nitrate solution with a neutral pH (pH = 7), the best indicator for this titration would be p-Nitrophenol (pK_a 7.2).

12. B

A buffer solution is a solution of a weak acid and its conjugate base. Buffer solutions stabilize the pH near the pK_a of the weak acid. A buffer absorbs excess protons or hydroxide into the equilibrium between the weak acid and weak base. To determine the pH of a buffer solution, we use the Henderson-Hasselbalch equation.

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

The first step is to convert the K_a of carbonic acid into its pK_a . On the MCAT feel free to use the approximation method. Make the negative exponent a positive whole number and subtract $\frac{1}{10}$ of the coefficient from this whole number. This will get us close enough for the MCAT.

$$pK_{a} = -\log(4.4 \times 10^{-7}) \sim 7 - 0.44 \sim 6.6$$

If the concentration of the weak acid in a buffer is ten times the concentration of the base, the pH will be a full point lower than the pK_a of the acid.

pH ~ 6.6 + log
$$\left(\frac{0.1}{1.0}\right)$$

pH ~ 5.6

When you approximate pK_a , you shouldn't be surprised to land a few tenths of a point off in your answer. (The common logarithm of 4.4 is actually 0.64 not 0.44.) The MCAT almost never spaces quantitative answer choices near to one another. They want to encourage mental math.

13. C

HCl is a strong acid. K_2CO_3 is a strong electrolyte. Both will completely dissociate.

HCl
$$\rightarrow$$
 Cl⁻ + H⁺
K₂CO₃ \rightarrow 2K⁺ + CO₃²

Excess H^+ will drive the carbonate to carbonic acid.

$$\mathrm{CO}_3^{2-} + \mathrm{H}^+ \longrightarrow \mathrm{HCO}_3^{-}$$

 $\mathrm{HCO}_3^{-} + \mathrm{H}^+ \longrightarrow \mathrm{H}_2\mathrm{CO}_3^{-}$

Carbonic acid decomposes to form carbon dioxide gas and water. This is one of the MCAT's favorite reactions.

$$H_2CO_3(aq) \rightarrow CO_2(g) + H_2O$$

14. D

It is axiomatic in general chemistry that nonmetal oxides react with water to form acids, and metal oxides react with water to form bases. Of our choices, three are nonmetal oxides. These will form acids in water.

$$CO_{2} + H_{2}O \rightleftharpoons H_{2}CO_{3}$$
$$SO_{2} + H_{2}O \rightleftharpoons H_{2}SO_{3}$$
$$P_{4}O_{10} + 6H_{2}O \rightleftharpoons 4H_{3}PO_{4}$$

Calcium oxide is a metal oxide. It forms a base in water.

$$CaO + H_2O \rightleftharpoons Ca(OH)_2$$

15. A

HF is the only hydrohalic acid that isn't classified as a strong acid. When HF dissociates the hydronium ion remains attached to F^- , so HF is functionally a weak acid.

16. A

As a general rule with oxygen acids, the greater the number of oxygens around the central atom, the stronger the acid. Not only will there be greater inductive pull from the oxygens polarizing the O–H bond, there will be more resonance forms to stabilize the conjugate base.

17. C

A crucial application of the Henderson-Hasselbalch framework in biochemistry is to understand how physiological pH (7.4) dictates the state of ionization of biomolecules. The ratio of protonated to unprotonated forms will adjust to the pH.

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

Substituting the values for the lysine side-chain, we can see that at physiological pH, lysine will be protonated at approximately 1000:1 ratio.

$$7.4 = 10.5 + \log \left(\frac{[lys - NH_2]}{[lys - NH_3^+]} \right)$$
$$\log \left(\frac{[lys - NH_2]}{[lys - NH_3^+]} \right) = -3.1$$
$$\frac{[lys - NH_2]}{[lys - NH_3^+]} = \frac{1}{1000}$$

18. A

The salt bridge stabilizes acid form of the histidine residue and the base form of aspartate.



If the acid form of histidine is more stable, the surroundings will push protons onto histidine more easily. The histidine will more likely be protonated. The pK_a of the side chain of a free histidine in

aqueous solution is 6.0. At physiological pH this would mean only 1:25, approximately, are protonated. This salt bridge stabilizing the conjugate acid has raised the pK_a above physiological pH, so now the majority of the time a histidine residues will be protonated.

The same logic applies to the lowering of the pK_a of the aspartate residue. The salt bridge stabilizes the carboxylate form. However, this is not so significant biochemically because aspartate is already a reliable negative. The pK_a of the side chain of a free aspartate is 3.8. In other words, at physiological pH, nearly all aspartate side chains are deprotonated, so lowering the pK_a even further produces no big effect.

Conversely, the change in the pK_a of the histidine is very significant biochemically and physiologically. It's the molecular basis for the Bohr effect, the decrease in the affinity of hemoglobin for oxygen at lower pH. The deoxygenated form is stabilized in the tissues where CO₂ production has lowered pH. Oxygen unloads as protons load onto hemoglobin.

19. B

The titration of a weak acid with a strong base involves the strong base converting the weak acid into weak base. For example, if we were titrating acetic acid with sodium hydroxide, we would be forming sodium acetate.

$$HC_2H_3O_2 + NaOH \rightarrow NaC_2H_3O_2 + H_2O$$

At the equivalence point we would have added exactly as many equivalents of NaOH as $HC_2H_3O_2$, and we would have produced a solution of Na- $C_2H_3O_2$. Up to that point, though, our solution would constitute a mixture of $HC_2H_3O_2$ and Na- $C_2H_3O_2$. A solution which is a mixture of a weak acid and its conjugate base is a buffer solution. We can see from the Henderson-Hasselbalch equation that at the half equivalency point, when the concentrations of the weak acid and base are equal, the pH of the solution would be equal to the pK_a of the weak acid.

$$\mathrm{pH} \;=\; \mathrm{p}K_{\mathrm{a}} \;+\; \log\left(\frac{\mathrm{[A^-]}}{\mathrm{[HA]}}\right)$$

In the titration of a weak acid with a strong base, you can determine the pK_a of the weak acid by inspection of the titration curve. The pH halfway to the equivalence point equals the pK_a .



20. C

The answer choices exemplify a commonly employed format representing amino acid substitutions. 'A123D' signifies that an alanine was changed to aspartate at position 123 in the primary structure.

The isoelectric point, pI, of a protein, is the pH at which the most likely state of ionization of the protein is electrically neutral, so the protein does not migrate in an electric field if the pH of its solution environment equals its isoelectric point.

It helps to understand isoelectric point to picture an acidic solution environment as a kind of proton pressure onto the protein and a basic solution environment as a kind of pull that removes protons from the protein. A protein with a large proportion of aspartate and glutamate will be negatively charged at neutral pH. It will have a low isoelectric point because it requires an acidic pH to push protons onto the protein and make those negative charges neutral. Likewise, a protein with a large proportion of lysine or arginine will have a high
isoelectric point. It will be positively charged at neutral pH, and it requires the pH to be more basic to pull the protons off of those residues and render the protein neutrally charged.

Of our answer choices, the substitution that would be expected to produced the greatest decrease in the isoelectric point is K299E. We are removing a positively charged residue (K = lysine) and replacing it with a negatively charged residue (E = glutamate). Instead of pulling a proton off to neutralize the residue, we would have to push a proton on, so the isoelectric point will now be more acidic.

One thing to mention. If you missed this question because you don't know the single letter codes for the amino acids, it might be a good time to start hitting those, even if you haven't gotten to biochemistry in content review. The MCAT will give you a bad time if you don't know those backwards and forwards.

Redox & Electrochemistry Practice Items

- 1. An oxidizing agent
 - A. receives electrons in a redox reaction.
 - **B.** supplies electrons in a redox reaction.
 - **C.** tends to contain atoms with low oxidation numbers.
 - **D.** reacts spontaneously with O_2 .
- 2. What is the oxidation number of chlorine in dichlorine heptoxide?



- **A.** -4
- **B.** 0
- **C.** +4
- **D.** +7
- **3.** Which of the following statements is true regarding the reaction of copper(II) sulfate with iron?

 $Fe(s) + CuSO_4(aq) \longrightarrow FeSO_4(aq) + Cu(s)$

- I. Iron is reduced
- II. Copper is reduced
- III. Sulfate ion serves as an oxidizing agent
- A. I only
- **B.** II only
- C. I and III
- **D.** II and III

- 4. Which of the following is true regarding molecular oxygen and molecular hydrogen?
 - **A.** O_2 is usually reduced in reaction (not with fluorine), while H_2 is usually oxidized (though not by metals).
 - **B.** The oxidation number of oxygen in O_2 is -2, while the oxidation number of hydrogen in H_2 is +1.
 - C. O_2 is a strong reducing agent, while H_2 is usually an oxidizing agent.
 - **D.** Hydrogen gas production from a reaction vessel is often the result of the reduction of a metal.
- 5. Which of the following metals will react vigorously with liquid water to give H₂?
 - **A.** Ag **B.** Au **C.** Hg **D.** L
- 6. Potassium permanganate, $KMnO_4$, is a strong oxidizing agent. In reactions with potassium permanganate, which atom is reduced?
 - **A.** K
 - B. Mn
 - **C.** O
 - **D.** The substrate is reduced.
- 7. Many pure metals can be produced by reaction of their chlorides with sodium because
 - A. sodium forms an ionic compound with chlorine.
 - **B.** sodium ion possesses a very high negative standard reduction potential.
 - C. sodium is a very electrophilic element.
 - **D.** sodium chloride has a large lattice energy.

8. What is the coefficient on chlorine molecule when the following oxidation reduction reaction (in acidic solution) is balanced?

$$\operatorname{Cr}_2O_7^{2-} + \operatorname{Cl}^- \longrightarrow \operatorname{Cr}^{3+} + \operatorname{Cl}_2$$

- **A.** 1
- **B.** 3**C.** 6
- **D.** 7
- **D.** /
- **9.** In the reaction below, which species is oxidized and which is reduced?

$$NH_4 + NO_2 \longrightarrow N_2 + 2H_2O$$

- A. H is oxidized and N is reduced.
- **B.** N is oxidized and O is reduced.
- C. N is both oxidized and reduced.
- **D.** N is oxidized and H is reduced.
- **10.** A large, positive standard reduction potential for a substance indicates that the substance is
 - A. a strong reducing agent.
 - **B.** a strong oxidizing agent.
 - C. easily oxidized.
 - **D.** a cation.
- **11.** In an electrolytic cell
 - A. oxidation occurs at the positive anode.
 - **B.** reduction occurs at the positive anode.
 - C. oxidation occurs at the negative anode.
 - **D.** reduction occurs at the negative anode.

- **12.** In a galvanic cell
 - A. oxidation occurs at the positive anode.
 - **B.** reduction occurs at the positive anode.
 - C. oxidation occurs at the negative anode.
 - **D.** reduction occurs at the negative anode.
- **13.** Which of the following results from the electrolysis of a solution of 5M sodium chloride?
 - I. production of sodium at the anode and chlorine gas at the cathode
 - II. production of chlorine gas at the anode and hydrogen gas at the cathode
 - III. a basic solution around the cathode
 - A. I only
 - **B.** II only
 - C. I and III
 - **D.** II and III
- **14.** The anode and cathode reactions are as follows:

$$Zn(s) + 2OH^{-}(aq) \longrightarrow Zn(OH)_{2}(s) + 2e^{-}$$

$$Ag_{2}O(s) + H_{2}O + 2e^{-} \longrightarrow 2Ag(s) + 2OH^{-}(aq)$$

The standard reduction potential of Zn^{2+} is -0.762 V, and that of Ag⁺ is +0.800 V. What is the approximate emf of a silver oxide battery?

- **A.** 0.04 V**B.** 0.8 V
- **C.** 1.6 V
- **D.** 2.4 V

- 15. A battery runs dead when the redox reaction
 - **A.** has moved charge through the salt bridge equaling capacitance times voltage.
 - **B.** has consumed all available reagents.
 - **C.** has led to creation of an equal and opposite potential in the salt bridge.
 - **D.** reaches the equilibrium state.
- 16. Placing metallic zinc into a solution of 1M $CuCl_2$ will result in a layer of copper being deposited on the zinc. Placing an aluminum rod in a 1M solution of $ZnCl_2$ will result in metallic zinc being deposited on the aluminum. Which of the following can be concluded from these observations?
 - I. Zinc is a stronger reducing agent than copper.
 - II. The standard reduction potential of copper is more positive than that of zinc.
 - III. Copper ions would spontaneous-

ly

oxidize aluminum.

- A. I only
- **B.** II only
- C. I and III
- **D.** I, II and III
- 17. Commercial aluminum is formed electrolytically from aluminum oxide (Al_2O_3) , which is reduced at the cathode. Approximately how long must a current of 1000A be applied to form 50 g of aluminum?
 - A. 1 second
 - **B.** 1 1/2 minutes
 - C. 10 minutes
 - **D.** 17 hours

The following passage pertains to questions 18 - 22.

Thiamine pyrophosphate (TPP) is a thiamine (vitamin B1) derivative consisting of a pyrimidine ring which is connected to a thiazole ring, which is in turn connected to a pyrophosphate (diphosphate) functional group.



TPP performs an essential role in the catalytic activity of a number of enzymes. TPP is synthesized in the mitochondria for the activity of the pyruvate dehydrogenase complex (PDC). PDC is a complex of three enzymes that converts pyruvate into acetyl-CoA. This complex links glycolysis to the citric acid cycle. IN the mechanism of the pyruvate dehydrogenase enzyme, the anionic C2 carbon of TPP performs a nucleophilic attack on the C2 carbonyl of pyruvate. The resulting hemithioacetal undergoes decarboxylation.



of the dihydrolipoyl transacetylase enzyme of the complex. In a ring-opening SN2-like mechanism, the second sulfur is displaced as a sulfide. Release of the TPP cofactor and generates a thioacetate on lipoate. This is the rate-limiting step of the whole pyruvate dehydrogenase complex.

At this point, the lipoate-thioester functionality is translocated into the dihydrolipoyl transacetylase active site, where a transacylation reaction transfers the acetyl from the "swinging arm" of lipoyl to the thiol of coenzyme A. This produces acetyl-CoA, which is released from the enzyme complex and subsequently enters the citric acid cycle.



The dihydrolipoate, still bound to a lysine residue of the complex, then migrates to the dihydrolipoyl dehydrogenase active site where FAD converts dihydrolipoate back to its lipoate resting state, producing FADH₂. Then, a NAD⁺ cofactor converts FADH₂ back to its FAD resting state, producing NADH.



- **18.** Which of the following describes the activity of NAD⁺ in the dihydrolypoyl dehydrogenase mechanism.
 - I. oxidizing agent
 - II. reducing agent
 - III. Brønsted base
 - A. I only
 - **B.** II only
 - C. I and III
 - **D.** I, II and III
- **19.** In the dihydrolypoyl transacetylase mechanism, the conversion of the disulfide into the dithiol form of lipoamide produces which change in the oxidation state of each sulfur atom?

A.
$$-1$$
 to -2

- **B.** 0 to −1
- **C.** 0 to −2
- **D.** 0 to +1

- **20.** Which is a net result of the mechanism of pyruvate dehydrogenase complex?
 - **A.** Flavin is oxidized and nicotinamide is reduced.
 - **B.** Sulfur is oxidized and flavin is reduced.
 - **C.** Carbon is oxidized and nicotinamide is reduced.
 - **D.** Sulfur is oxidized and nicotinamide is reduced.
- **21.** The standard reduction potential, E° , of lipoamide disulfide is -0.29V. The standard reduction potential of NAD⁺ is -0.32V. Which of the following is necessarily true regarding the mitochondrial concentrations of these species during aerobic metabolism?
 - A. [NAD⁺][lipoamide dithiol] > [NADH] [lipoamide disulfide]
 - **B.** [NAD⁺][lipoamide disulfide] > [NADH][lipoamide dithiol]
 - C. [FAD][NADH] > [lipoamide dithiol] [NAD⁺]
 - D. [lipoamide dithiol][lipoamide disulfide] > [NAD⁺][FAD]
- **22.** The carbon atom of the carboxyl group of pyruvate will be oxidized, becoming CO_2 through the mechanism of the pyruvate dehydrogenase enzyme of the complex. What is the oxidizing agent?
 - **A.** thiamine pyrophosphate
 - **B.** lipoamide dithiol
 - C. another carbon of pyruvate
 - **D.** coenzyme A

Redox & Electrochemistry

Answers and Explanations

1. A

Redox is an accounting system. The valence electrons in a molecular, atomic or ionic species are all assigned to an element. Electrons within a covalent bond are assigned to the more electronegative element. This accounting system provides a useful way to keep track of how electrons shift from their old neighborhoods in the reagents to their new neighborhoods in the products. An electron which before was in the vicinity of a lithium atom now finds itself in the vicinity of a fluorine atom. It has fallen down into a well. An oxidizing agent (oxidant, oxidizer) is a substance that has the ability to oxidize other substances — in other words to accept their electrons.

2. D

There are two tracks you can choose from in assigning oxidation numbers. You can use the rules for assigning oxidation numbers, or if you know or are given the structural formula, you can think of each bond as a tug of war and assign the electrons brought to the bonds to the more electronegative element.

In our molecule, each chlorine has brought seven valence electrons to share with oxygen in covalent bonding. Although they are both very electronegative elements, oxygen is more electronegative than chlorine (3.5 vs. 3.0), so the electrons chlorine brought to these bonds become oxygen's property in terms of redox accounting. The bond is only slightly polar, but we say those electrons are oxygen's. That's redox accounting. Oxygen has gained and chlorine has lost. Chlorine's oxidation number here is +7.

Alternatively, we could have used rules. One of our rules is that the oxidation number of oxygen is almost always -2. Another rule is that the sum of oxidation numbers in an electrically neutral molecule is 0. We have seven oxygens. $7 \times -2 = -14$,

so the two chlorines must be +7 each. Rules might be confusing though, because another rule is that the oxidation number of chlorine is almost always -1. One of the exceptions is that when it is bonded to oxygen.

3. B

In the reaction, copper's oxidation number changes es from +2 to 0. Iron's oxidation number changes from 0 to +2. Copper is reduced and iron is oxidized. Copper is the oxidizing agent and iron is the reducing agent.

4. A

In most reactions with O_2 , the oxygen atoms gain electron control over electrons brought by less electronegative elements to the reaction. In many reactions with H₂ hydrogen atoms lose electron control to more electronegative atoms. However, hydrogen's electronegativity is actually pretty respectable (2.1), so H₂ will not be readily oxidized by any metal.

5. D

It's very important to understand that hydrogen in its +1 oxidation state, such as in water or with H⁺ ions, can perform as a decent oxidizing agent. It's easy to forget in the world of organic chemistry, where everything is oxidizing hydrogen, that hydrogen, itself, actually has a respectable electronegativity (2.1), especially compared to metals. If a very reactive, ie. low electronegativity, metal such as lithium is exposed to water, a vigorous reaction will result in which hydrogen oxidizes lithium.

$$2\text{Li}(s) + 2\text{H}_2\text{O} \rightarrow 2\text{LiOH}(aq) + \text{H}_2(g)$$

The other metals of our answer choices are among the more electronegative transition metals. They are too electronegative to be oxidized by hydrogen.

6. B

Potassium permanganate is widely used as a strong oxidizing agent. The manganese atom has a high positive reduction potential. In a +7 oxidation state, its valence shell is all oxygen's property in KMnO_4 . The manganese atom is reduced (+7 to +2) when potassium permanganate oxidizes a substrate, such as oxidation of acetaldehyde to acetic acid below.

5 CH₃CHO + 2 KMnO₄ + 3 H₂SO₄ \rightarrow 5 CH₃COOH + 3 H₂O + K₂SO₄ + 2 MnSO₄ 7. **B**

A representative reaction of the type mentioned in the question stem would be sodium metal reacting with aluminum chloride to produce sodium chloride and aluminum. Aluminum oxidizes the sodium.

$$3 \operatorname{Na}(s) + \operatorname{AlCl}_{3}(aq) \longrightarrow 3 \operatorname{NaCl}(aq) + \operatorname{Al}(s)$$

With electronegativity of 1.61, you would not normally expect to see aluminum oxidizing anything, but sodium's electronegativity is even lower, 0.93. In a tug-of-war with sodium over electrons, aluminum wins.

In other words, sodium is a great reducing agent. The best, most precise way to say that something is a powerful reducing agent is to say that its oxidized form, here sodium ion, has a large negative standard reduction potential.

$$Na^+(aq) + e^- \longrightarrow Na(s)$$
 $E^0 = -2.71V$

This means that if you were removing electrons from a standard hydrogen electrode and trying to put them onto sodium ions, the electrons would have a long uphill climb to get there, 2.71 joules to climb up for every coulomb of electrons.

Think of the standard hydrogen electrode as the ground floor of a house. Some other places an electron might find itself are like the roof of the house. These are reducing agents like sodium, lithium or potassium. Reducing agents have negative standard reduction potential. Electrons have an uphill climb to get to these from the hydrogen electrode. Some other places are like the basement of the house, such as fluorine or oxygen. These are oxidizing agents. Oxidizing agents have positive standard reduction potential.

Aluminum itself has a substantial negative standard reduction potential.

$$Al^{3+}(aq) + 3e^{-} \rightarrow Al(s) \quad E^{0} = -1.66V$$

Even though aluminum itself is a decent reducing agent, it will oxidize sodium because the trip for an electron from sodium to aluminum is downhill -2.71V to -1.66V.

8. B

Balancing by oxidation number method begins by determining the change in oxidation states of all of the individual species in the reaction and then balancing the increase with the decrease. The oxidation number decrease (minus 6 total), in chromium, is balanced with the increase, in chlorine (+6), when the coefficients are as follows.

$$Cr_2O_7^{2-} + 6Cl^- \rightarrow 2Cr^{3+} + 3Cl_2$$

The above is sufficient to answer the question, but let's look at the finished balanced reaction after inclusion of water and hydrogen ions.

$$14\mathrm{H}^{+} + \mathrm{Cr}_{2}\mathrm{O}_{7}^{2-} + 6\mathrm{Cl}^{-} \rightarrow 2\mathrm{Cr}^{3+} + 3\mathrm{Cl}_{2} + 7\mathrm{H}_{2}\mathrm{O}$$

Though balancing redox reactions ia a classic Chem 101 problem, it's not a typical MCAT exercise. It's important to see and understand how this kind of thing works. It's important to understand that the oxidation number increase in a redox reaction must be matched by an oxidation number decrease.

9. C

Disproportionation is a redox reaction in which one compound of intermediate oxidation state converts to two compounds, one of higher and one of lower oxidation states. As an example, phosphorous acid disproportionates upon heating to give phosphoric acid and phosphine.

$$4 H_3 PO_3 \rightarrow 3 H_3 PO_4 + PH_3$$

The reaction in the problem is the reverse of a disproportionation. A substance is formed, N_2 , in an intermediate oxidation state from precursors of lower and higher oxidation states. The reverse of disproportionation is called comproportionation.

10. B

Fluorine is an example of a substance with a large positive standard reduction potential. It is a powerful oxidizing agent.

 $F_2 + 2e^- \longrightarrow 2 F^- \qquad E^0 = +2.87V$

This means that if you removed electrons from a standard hydrogen electrode and gave them to fluorine, the electrons would fall down into a deep well of binding energy, 2.87 joules for every coulomb of electrons.

11. A

Oxidation always occurs at the anode, whether the cell is electrolytic or galvanic. The reaction occurring in an electrolytic cell is non-spontaneous. An external voltage is being applied to make the reaction occur. What this means is that the electrons are being pushed uphill by the voltage, the overall cell potential being negative. Uphill for electrons is the journey from a positive potential to a negative potential. The external voltage is pulling the electrons out from the positive anode, where oxidation is occurring, and pushing them up onto the negative cathode, where reduction is occurring.

12. C

Oxidation always occurs at the anode, whether the cell is electrolytic or galvanic. The reaction occurring in an electrolytic cell is spontaneous. Electrons are falling downhill. The overall cell potential is positive. Downhill for electrons is the journey from a negative anode, where oxidation is occurring, to a positive cathode, where reduction is occurring.

13. D

Electrolysis of brine (concentrated NaCl) will oxidize Cl⁻ ions at the anode forming Cl₂. The only other possible reductant would be the oxygen in water (hydrogen and sodium are already oxidized). Oxygen is generally more electron greedy than chlorine. In other words, it has a higher positive standard reduction potential than chlorine, so the voltage will pull the electrons from chloride preferentially over oxygen. Therefore, the anode half reaction is as follows.

$$2 \operatorname{Cl}^{-}(\operatorname{aq}) \longrightarrow \operatorname{Cl}_{2}(g) + 2e^{-}$$

At the cathode, the question of whether hydrogen or sodium will be reduced is easy. Sodium ions have a big negative standard reduction potential while hydrogen, of course, has a standard reduction potential of zero. It's the ground floor we compare everything to. Compared to hydrogen, sodium ions are a place it takes 2.71 joules of energy to move a coulomb of electrons to from a standard hydrogen electrode.

$$Na^+(aq) + e^- \longrightarrow Na(s)$$
 $E^0 = -2.71V$

Compared to sodium, in other words, hydrogen is a very respectable oxidizing agent, so hydrogen is reduced at the cathode, not sodium.

$$2 \text{ H}_{2}\text{O} + 2e^{-} \rightarrow 2 \text{ OH}^{-}(\text{aq}) + \text{H}_{2}(\text{g})$$

In summary, electrolysis of brine produces chlorine gas at the anode and hydrogen gas at the cathode. As the reaction progresses, the solution forms concentrated sodium hydroxide.

14. C

The standard reduction potential represents the path that electrons would take from a standard hydrogen electrode to reduce a particular oxidant.

The standard reduction potential of Zn^{2+} tells us that for hydrogen to reduce Zn^{2+} ions, electrons would need to travel uphill from hydrogen to -0.762 V. To reduce Ag⁺ the electrons would travel downhill, though, from hydrogen to +0.800 V.

If you think about it, these two standard reduction potentials respectively have given us the two legs of the journey all the way from Zn (the reductant in our cell) to Ag⁺ (the oxidant). Instead of going uphill to Zn²⁺, we imagine going in the reverse, downhill instead from Zn to hydrogen. Instead of uphill to Zn²⁺, downhill to hydrogen would be a change in the +0.762 V direction, and then from hydrogen to Ag⁺, which would be another +0.800 V, so our cell potential is approximately 1.6V (0.762 V + 0.800 V). Don't let this be complicated. The electrons are falling from -0.762 V to +0.800 V.

The way you say this imaginary path as a formula is as follows.

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

15. D

One of the fundamental conceptual leaps we make into electrochemistry is to conceive of the free energy change in a chemical reaction as the journey of electrons through a potential difference. Instead of joules per mole we think in terms of joules per coulomb, or volts, as electrons transfer from the reductant to the oxidant. Underlying both conceptual frameworks is the fundamental reality that internal energy change in chemical reactions derive from the electrostatic potential energy differences as valence electrons find themselves within the new structural configurations of the product. Electrons were adjacent to a carbon atom and now they are in a covalent bond being pulled towards an oxygen nucleus, for example. For an oxidation-reduction reaction, we can convert a cell potential into a free energy change by using the Faraday unit for conversion of moles of electrons into Coulombs.

 $1 F = 96,500 \text{ C mol}^{-1}$ $\Delta G = -nFE$

A very important equation in chemical thermodynamics describes how the free energy change of a reaction, ΔG , depends on both the standard free energy change, ΔG° , and the reaction quotient, Q.

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

In other words, whether a reaction is spontaneous in the forward or reverse direction depends not only on how the free energies of the product and reagent would compare, ΔG° , if they were both present in equal concentration. It also depends on what their concentrations actually are in the beaker, the reaction quotient, Q. A reaction with a negative standard free energy change, spontaneous forward if product and reagent are in equal concentration, may even run in the reverse direction if there is a high concentration of product and very little reagent.

We can convert this equation into a form which is convenient for electrochemistry. This new form of our thermodynamics equation is called the Nernst equation.

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$

- $nFE_{cell} = -nFE_{cell}^{\circ} + RT \ln Q$
$$E_{cell} = E_{cell}^{\circ} - \frac{RT}{nF} \ln Q$$

$$E_{cell} = E_{cell}^{\circ} - \frac{0.0592V}{n} \ln Q$$

The actual cell potential depends not only on how the standard reduction potentials of the product and reagent sides of the reaction compare, E° , the cell potential if they were both present in equal concentration. The cell potential also depends on what their concentrations actually are in the electrochemical cell, which is given by the reaction quotient, Q. As a redox reaction proceeds towards equilibrium , $Q \longrightarrow K$, the free energy change approaches zero, $\Delta G \longrightarrow 0$, and, equivalently, the cell potential approaches zero, $E_{cell} \longrightarrow 0$.

In summary, a dead battery is a chemical reaction that has attained the equilibrium state.

16. D

The evidence presented in the question stem is consistent with the relative standard reduction potentials of copper, zinc, and aluminum. On the table of standard reduction potentials below, we can see that aluminum metal is a stronger reducing agent than zinc metal which, in turn, is a stronger reducing agent than copper metal, and, equivalently, a copper ion is a stronger oxidizing agent than a zinc ion, which, in turn, is a stronger oxidizing agent than an aluminum ion. The standard reduction potential of a substance tells you the energy involved in reduction of the substance by the standard hydrogen electrode. The more negative the standard reduction potential, the more uphill the trip electrons must take in terms of potential energy. The more positive the standard reduction potential, the further downhill the electrons are falling from hydrogen to carry out the reduction of the substance.

In the question stem, we were told that placing metallic zinc into a solution of $1M \operatorname{CuCl}_2$ will result in a layer of copper being deposited on the zinc. When metal ions are reduced, they 'plate out' as pure metal. This happens spontaneously because zinc is a stronger reducing agent than copper (choice I), ie. it has a more negative reduction potential than copper; copper has a more positive reduction potential than zinc (choice II).

Additionally, we were told that placing an aluminum rod in a 1M solution of $ZnCl_2$ will result in metallic zinc being deposited on the aluminum. This tells us that aluminum has a more negative reduction potential than zinc. If aluminum has a more negative reduction potential than zinc and zinc has a more negative reduction potential than copper, aluminum must through transitive principle have a more negative reduction potential than copper. It follows that copper ions would spontaneously oxidize aluminum.

E° (V)						
-2.93		К+	+	e ⁻		к
-2.71		Na ⁺	+	e ⁻		Na
-1.66		Al ³⁺	+	3 e		AI
-0.76		Zn ²⁺	+	2 e ⁻		Zn
-0.44		Fe ²⁺	+	2 e ⁻		Fe
-0.25		Ni ²⁺	+	2 e-		Ni
0		2 H+	+	2 e ⁻		H ₂
+0.16		Cu ²⁺	+	2 e"		Cu
+0.77		Fe ³⁺	+	e ⁻		Fe ²⁺
+0.80	_	Ag ⁺	+	e ⁻		Ag
+1.23	0 ₂ +	4 H*	+	4 e ⁻		H ₂ O
+1.36		CI ₂	+	2 e ⁻		CI-
+1.51	MnO ₄	+ 8	3 H+	+ 5 e ⁻		Mn ²⁺ + 4H ₂ O
+2.08	03	+ 2	2 H+	+ 2 e	-	0 ₂ + 4H ₂ O
+2.87		F_2	+	2 e ⁻	-	F-

17. C

It's unlikely to have a version of this type of problem on the MCAT involving extensive quantitative work, but you need to know how to get through a basic form. The key to relating the chemical stoichiometry of a redox reaction to DC current parameters is the conversion factor known as *the Faraday*.

$$F = 96,500 \text{ C mol}^{-1}$$

1

A mole of electrons is the same as 96,500 coulombs of electric charge.

We're making 50g of Al (s). The atomic weight of Al is 27g mol⁻¹. Let's start rolling out conversion factors. This gets us to moles of aluminum.

50g AI
$$\left(\frac{1 \text{ mol Al}}{27 \text{ g Al}}\right)$$

Aluminum in Al_2O_3 is in the +3 oxidation state. To plate out 1 mole of aluminum requires 3 moles of electrons.

$$Al^{3+} + 3e^{-} \rightarrow Al$$

This gets us to moles of electrons.

$$50g AI \left(\frac{1 \text{ mol Al}}{27 \text{ g AI}}\right) \left(\frac{3 \text{ mol } e^{-}}{1 \text{ mol AI}}\right)$$

Now the Faraday to get to electric charge.

$$50g \text{ AI}\left(\frac{\text{mol AI}}{27 \text{ g AI}}\right)\left(\frac{3 \text{ mol }e^{-}}{\text{mol AI}}\right)\left(\frac{96,500 \text{ C}}{\text{mol }e^{-}}\right)$$

We were given that the current employed is 10,000A. If 1,000 coulombs flow per second, there is one second per 1,000 coulombs.

$$50 \text{g AI}\left(\frac{\text{mol AI}}{27 \text{ g AI}}\right) \left(\frac{3 \text{ mol } \text{e}}{\text{mol AI}}\right) \left(\frac{96,500 \text{ C}}{\text{mol } \text{e}}\right) \left(\frac{1 \text{ s}}{1,000 \text{ C}}\right)$$

At the start, you don't need to see the whole solution to your foothold with a problem like this. Feel your way. We've worked through conversion factors all the way from grams of aluminum to the time required. Our answers are well spaced, so let's call $\frac{5}{27} \sim 2$ and $96,500 \sim 100,000$.

$$50g \text{ AI}\left(\frac{\text{mol} \text{ AI}}{27 \text{ g} \text{ AI}}\right) \left(\frac{3 \text{ mol} \text{ e}^{-}}{\text{mol} \text{ AI}}\right) \left(\frac{96,500 \text{ C}}{\text{mol} \text{ e}^{-}}\right) \left(\frac{1 \text{ s}}{1,000 \text{ C}}\right)$$
$$\sim 600 \text{ s}$$

18. D

NAD⁺ oxidizes FADH₂. It is an oxidizing agent. Oxidation by NAD⁺ always involves a two electron transfer in the form of a hydride (H^-).

Note that even though a hydrogen is transfered, it is not a proton transfer, but a hydride transfer. NAD⁺ is not acting as a Brønsted base.

19. A

In lipoamide disulfide, each sulfur has one covalent bond to a carbon and one to a sulfur. Sulfur is slightly more electronegative than carbon (2.6 to 2.5), so the electron that carbon brought to that bond are assigned in redox accounting to sulfur. In lipoamide disulfide the oxidation state of sulfur is therefore -1.

In the dithiol form of lipoamide, each sulfur has one covalent bond to a carbon and one to a hydrogen. Sulfur is more electronegative than both carbon and hydrogen, so each of the electrons those respective atoms brought to these bonds are now sulfur's property. In the dithiol form the oxidation state of sulfur is therefore -2.

Not only in the context of lipoamide, but also regarding disulfide bridges in proteins and other important contexts such as the activity of glutathione, it's very important in biochemistry to recognize the disulfide form as the oxidized form and the dithiol as the reduced form.

20. C

As a result of the reactions of the pyruvate dehydrogenase complex, a pair of electrons that had been the property of carbon (originally within the nutrient molecule glucose) have become the property of nicotinamide. Between pyruvate and NADH, the pair of electrons were passed first to the two sulfurs of lipoamide, which then passed them to the flavin of FAD. FAD then passed them to NADH. Subsequent to completion of the mechanism, both lipoamide and FAD have returned to their initial oxidized state. In the net mechanism, carbon has been oxidized and NAD⁺ reduced.

21. A

For of lipoamide disulfide to have a standard reduction potential of -0.29V means we would need to be pushing electrons uphill to NAD⁺ at -0.32V, if the concentrations the reagents and products were all equal. In other words, the standard cell potential of a lipoamide/NAD cell would be -0.03V.

$$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$$

-0.03V = (-0.32V) - (-0.29V)

The reaction would not be spontaneous forward in that case. A negative standard cell potential corresponds to a positive standard free energy change.

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

However, just as the actual free energy change not only depends on the standard free energy change but also the reaction quotient, so does the cell potential, which we can see in the Nernst equation.

$$\Delta G = \Delta G^{\circ} + RT \ln Q$$
$$-nFE_{cell} = -nFE_{cell}^{\circ} + RT \ln Q$$
$$E_{cell} = E_{cell}^{\circ} - \frac{RT}{nF} \ln Q$$
$$E_{cell} = E_{cell}^{\circ} - \frac{0.0592V}{n} \ln Q$$

For the dihydrolipoyl dehydrogenase mechanism to be spontaneous forward, the reaction quotient must be a fraction. The product of the concentrations of the reagents [NAD⁺][lipoamide thiol] must be greater than the product of the concentrations of the reaction products [NADH][lipoamide disulfide].

22. C

Although a carbon of pyruvate is oxidized through the mechanism of the pyruvate dehydrogenase enzyme, at this stage of the overall pyruvate dehydrogenase complex there has not yet been any net movement of electrons from the nutrient carbons to the electron shuttling coenzymes. The carboxyl carbon has lost an electron which the original carbonyl carbon of pyruvate has gained, so this is a type of disproportionation in which one carbon converts to a higher oxidation state and one to a lower oxidation state.



Coordination Chemistry Practice Items

- 1. In the ferrocyanide ion, the six electrons ferrous ion possesses outside of the argon shell assort into three of the five 3d orbitals, and the two remaining 3d orbitals, one 4s orbital, and three 4p orbitals hybridize to form bond orbitals to receive cyanide electron pairs. The shape of the ferrocyanide ion is
 - A. trigonal planar
 - **B.** tetrahedral
 - **C.** trigonal bipyramidal
 - **D.** octahedral
- 2. A substance which may serve as a ligand in a coordination ion may best be described as a(n)
 - A. Lewis base
 - B. nucleophilic anion
 - C. transition metal
 - D. electrophilic cation
- 3. The two complex ions pictured below are
 - A. optical isomers
 - **B.** conformational isomers
 - C. geometric isomers
 - D. constitutional isomers



- 4. A test for silver ion is formation of a precipitate with chloride ion which is soluble in ammonium hydroxide solution. Which compound forms to allow AgCl to dissolve?
 - A. AgOH B. NH_4Cl C. $[Ag(NH_3)_2]^+$
 - **D.** AgBr
- **5.** Aqua regia is a mixture of nitric acid and hydrochloric acid that can dissolve gold.

Au + 3 HNO₃ + 4 HCl \longrightarrow

 $[\operatorname{AuCl}_4]^-$ + 3 NO₂ + H⁺ + 2 H₂O

What role does chloride play in the process of dissolving gold?

- A. conjugate base
- **B.** ligand
- C. oxidizing agent
- **D.** reducing agent
- 6. In aqueous solution, the Ti³⁺ cation exists as the octahedral hydrate $[Ti(H_2O)_6]^{3+}$. Titanium(III) has a single 3d electron. Because two of the d orbitals $(d_{x2-y2} \text{ and } d_{z2})$ are nearer to ligand electrons than the other three $(d_{xy}, d_{xz},$ and $d_{yz})$, an electron in either of the first two will experience a greater repulsion from ligand electrons. The energy difference for an electron between these two sets of d orbitals is termed the
 - A. crystal field splitting energy.
 - **B.** coordination energy.
 - C. HOMO to LUMO transition energy.
 - **D.** charge transfer transition energy.

- 7. Cobalt III forms many octahedral complexes. $[Co(NH_3)_6]^{3+}$ is yellow and $[Co(NH_3)_5Cl]^{2+}$ is violet. Which of the following is the best explanation for the difference in color?
 - A. the greater d-d transition energy in $[Co(NH_3)_6]^{3+}$.
 - **B.** $[Co(NH_3)_6]^{3+}$ is a high spin complex while $[Co(NH_3)_5Cl]^{2+}$ is low spin.
 - **C.** the bathochromatic shift due to greater HOMO to LUMO transition energy.
 - **D.** the difference in enthalpy of hydration.
- 8. $Cr_2(SO_4)_3$ is a soluble electrolyte. Dissolving $Cr_2(SO_4)_3$ yields a violet solution. Titrating with NaOH produces a blue-violet precipitate (Compound II). Upon further titration with additional base, the precipitate redissolves as Compound III. Which of the following is Compound III?
 - **A.** $[Cr(H_2O)_6]^{3+}$
 - **B.** $[Cr(H_2O)_4(OH)_2]^+$
 - **C.** $[Cr(H_2O)_3(OH)_3]$ **D.** $[Cr(H_2O)_2(OH)_4]^-$
- **9.** Tris(ethylenediamine)cobalt(III) chloride is the chloride salt of the complex ion $[Co(en)_3]^{3+}$ where 'en' is the abbreviation for the bidentate ethylenediamine ligand, pictured below.



What is the coordination number of cobalt in tris(ethylenediamine)cobalt(III) chloride?

- **A.** 2
- **B.** 3
- **C.** 6
- **D.** 8

10. We can arrange ligands in the order of their ability to produce large crystal field splitting energy, Δ . This series is called the spectro-chemical series.

 $Br^- < Cl^- < F^- < OH^- < H_2O < NH_3 < NO_2^- < CN^-$

Of the following ligands, which has the greatest possibility of producing a diamagnetic complex?

- A. NH₃
- **B.** Br⁻
- C. OH-
- **D.** Br⁻
- 11. The iron within the heme prosthetic group of deoxyhemoglobin is in Fe(II). After binding O_2 , the iron transfers a single electron to the oxygen, becoming Fe(III). In what form is the oxygen bound to oxyhemoglobin?
 - A. singlet oxygen
 - **B.** triplet oxygen
 - C. superoxide
 - **D.** ozone



The following passage pertains to questions 12 - 17.

Alpha-ketoglutarate-dependent hydroxylases are non-heme, iron-containing enzymes that consume oxygen and alpha-ketoglutarate as co-substrates. They catalyze a wide range of oxygenation reactions. Functionally, the α KG-dependent hydroxylases are comparable to cytochrome P450 enzymes, which use oxygen and reducing equivalents to oxygenate substrates. In both α KG-dependent hydroxylases and cytochrome P450 enzymes, a high-valent oxoiron(IV) intermediate, first formed through O₂ activation, abstracts a hydrogen from the substrate. The incipient substrate radical is then captured by a hydroxoferric intermediate to afford the hydroxylated product

A typical α KG dependent non-heme iron(II) dioxygenase, TauD, catalyzes the alpha-ketoglutarate-dependent hydroxylation of taurine yielding sulfite and aminoacetaldehyde after decomposition of an unstable intermediate. Expressed as a particular variant in *Escherichia coli* only under conditions of sulfate starvation, TauD is required for the utilization of taurine as an alternative sulfur source for growth in the absence of sulfate.

In the active site of TauD, the iron(II) center is coordinated facially by two histidines and one aspartate residue, a motif known as the '2-His-1-carboxylate facial triad'. The first step involves the binding of α KG and taurine to the active site. α KG coordinates to Fe(II) while the taurine substrate is held by noncovalent forces in close proximity.



Subsequently, molecular oxygen binds end-on to Fe cis to the two donors of the α KG. The uncoordinated end of the superoxide ligand attacks the keto carbon, inducing release of CO_2 and forming an Fe(IV)-oxo intermediate.



This Fe=O center then oxygenates the substrate by an oxygen rebound mechanism.



- **12.** Which of the following descriptors accurately characterizes the stereochemical relationship of the two histidine ligands of Fe(II) in the active site of TauD?
 - A. mer
 - **B.** cis
 - C. octahedral
 - **D.** chiral

- **13.** Which of the following binds to the iron co-factor of TauD as a bidentate ligand?
 - A. histidine imidazole
 - **B.** alpha-ketoglutarate
 - C. taurine
 - **D.** superoxide
- **14.** During the ternary complex formation stage of the Tau-D mechanism, the iron cofactor of Tau-D acts as a
 - A. Lewis acid
 - **B.** Lewis base
 - C. reducing agent
 - **D.** ligand

- **17.** Which of the following is a characteristic of the low spin d⁴ Fe(IV) cofactor attached to the oxo ligand?
 - I. diamagnetic
 - II. high crystal field splitting energy
 - III. tetrahedral geometry
 - A. I only
 - **B.** II only
 - C. I and II
 - **D.** I, II, and III

- 15. Many α KG-dependent dioxygenase enzymes catalyze uncoupled turnover, in which oxidative decarboxylation of α KG into succinate and carbon dioxide proceeds in the absence of substrate. Such enzymes would be dependent on a
 - A. cytochrome
 - **B.** heme cofactor
 - C. bridging ligand
 - **D.** reducing agent
- **16.** The His–Fe(II)–His bond angle in TauD in its unbound state is nearest to which of the following?
 - **A.** 60°
 - **B.** 90°
 - **C.** 109°
 - **D.** 120°

Coordination Chemistry

Answers and Explanations

1. D

The question stem describes a complex ion with coordination number of 6, six cyanide ligands arrayed around a central iron. As described in VSE-PR (valence shell electron pair repulsion), when there are six regions of electron density around a central atom, the resulting geometry is octahedral.



2. A

A ligand is an ion or molecule that binds to a central metal atom to form a coordination complex. The bonding with the metal generally involves the contribution of one or more of the ligand's electron pairs to forming the bond(s) to the metal. A ligand is a Lewis base, in other words, an electron pair donor.

3. C

An octahedral complex such as $[Co(NH_3)_4Cl_2]^+$ can exist in a type of stereoisomerism known as geometric isomerism. Geometric isomers are each of two or more compounds which differ from each other in the arrangement of groups with respect to a double bond, ring, or other rigid structure. Just as with geometric isomerism in organic chemistry, in coordination chemistry we can also use the pre-fixes "cis" and "trans", from Latin, which mean "this side of" and "the other side of", respectively, to distinguish these two geometric isomers.



4. C

Dissolving a weak electrolyte can be facilitated through coupled equilibrium with complex ion formation.

5. D

Neither nitric acid nor hydrochloric acid will dissolve gold alone. Each acid performs a different task in combination in aqua regia. Nitric acid oxidizes gold to form a virtually undetectable concentration of gold ions (Au³⁺). The hydrochloric acid provides a ready supply of chloride ions (Cl⁻), which react with the gold ions to produce tetrachloroaurate(III) anions. In summary, nitric acid acts as an oxidizer and chloride as a ligand in complex ion formation, leading to the removal of gold ions from solution and allowing further oxidation of gold to take place.

6. A

In an octahedral complex, the d orbitals of the central metal ion divide into two sets of different energies. The separation in energy is the crystal field splitting energy.

7. A

Crystal field theory presents a simple model which is useful for explaining the observed color of many, though not all, coordination complexes. In crystal field theory, the ligand electron pairs create an electric field environment. The five d subshell orbitals of the central metal atom are not affected equally by this ligand field. Two of the five d-subshell orbitals in an octahedral complex, for example, are, basically, pressing against a ligand electron pair while the other three are not, so an electron in one of those two orbitals will be at a higher energy than within one of the other three. This is called crystal field splitting. Now that there is an energy difference among the d-subshell orbitals, there is an electronic transition which can correspond to photon absorbance. The absorbed photons tend to be visible.

We were told that the complex ion $[Co(NH_3)_6]^{3+}$ is yellow and $[Co(NH_3)_5Cl]^{2+}$ is violet. The color you see is not the color absorbed. You are seeing the complement of the color absorbed. If you see yellow, that means that violet photons are being absorbed, and vice versa. If you see violet color, it means yellow photons were absorbed. Violet photons are higher energy than yellow photons. This corresponds to the greater d-d transition energy in $[Co(NH_3)_6]^{3+}$

8. D

Many transition metal cations actually exist in aqueous solution as a hydrate complex ion. In solution chemistry, we say Cr^{3+} , but the actual form is $[Cr(H_2O)_6]^{3+}$.

The question gives us help in that the answer choices as a whole give us enough to construct the story. Titrating $[Cr(H_2O)_6]^{3+}$ (choice 'A') with base, we are replacing H_2O ligands with OH^- ligands. Eventually we reach $[Cr(H_2O)_3(OH)_3]$ (Compound II, choice 'C'), which is no longer an ion, and so it precipitates. Continuing to titrate with OH^- forms $[Cr(H_2O)_2(OH)_4]^-$ (Compound III, choice 'D'), which redissolves.

9. C

A bidentate ligand has two atoms that coordinate directly to the central atom in a complex. Ethylenediamine is a bidentate ligand. A single molecule of ethylenediamine can form two bonds to a metal ion. In tris(ethylenediamine)cobalt(III) chloride each of the three ethylenediamine ligands brings two electron pairs to cobalt(III), so the coordination number of cobalt is six, and it is an octahedral complex.

Although this is not an issue for the question, having three bidentate ligands, any tris(ethylenediamine)cobalt(III) complex is not super-imposable on its own mirror image, so there are two enantiomers of the complex.



10. C

 NH_3 is the ligand with the greatest ability to produce a complex with high splitting energy. In a complex with high crystal field splitting energy, the electrons will tend to pair in the lower energy d-subshell orbitals. High splitting energy is consistent with a low spin complex, in other words. If the splitting energy is low, though, there is a tendency for the electrons to go singly into all five orbitals with parallel spin as predicted by Hund's rule.

When there are six d-subshell electrons, a low spin complex will be diamagnetic (all electrons paired).



11. C

The behavior of heme in hemoglobin is one of the most significant examples of coordination chemistry in biochemistry. The oxygen in oxyhemoglobin is in the form of superoxide radical anion.



12. B

The passage describes the '2-His-1-carboxylate facial triad' in which the two histidine and one aspartate residues coordinate the Fe(II) cofactor facially. When three identical ligands occupy one face, the isomer is said to be facial, or fac. Facially oriented ligands within an octahedral complex will be cis to each other.



13. B

Bidentate ligands are Lewis bases that donate two pairs of electrons to a metal atom. αKG coordinates to Fe(II) as a bidentate ligand.



14. A

'Ternary complex' is not a term of conceptual vocabulary from coordination chemistry. It's not a kind of coordination complex but a kind of enzyme-substrate complex. A ternary complex is an enzyme-substrate complex formed between two substrate molecules and an enzyme. Multi-sub-strate enzyme-catalyzed reactions that follow a sequential mechanism will form a ternary complex. In other words, question stem is referencing is the initial substrate binding in which the iron cofactor receives the electron pairs brought by α KG as a coordinating ligand. A Lewis acid is an electron pair receiver.

15. D

Subsequent to decarboxylation of α KG the iron cofactor of an α KG-dependent dioxygenase will be in the Fe(IV) oxidation state. To complete the mechanistic cycle and return the iron to the Fe(II) oxidation state will require a reducing agent.

16. B

From VSEPR we know that the bond angles in octahedral geometry are 90° and 180° . The bond angle between two cis ligands in an octahedral complex is 90° .



17. B

In a complex with high crystal field splitting energy, the electrons will tend to pair in the lower energy d-subshell orbitals. In other words, high splitting energy produces a low spin complex.



Regarding choice 'I', even though the net spin is lower in this case than if the electrons had been spread out singly with parallel spin among the five d orbitals (high spin), low spin Fe(IV) is still paramagnetic. It would be diamagnetic only if all of the electrons were paired.