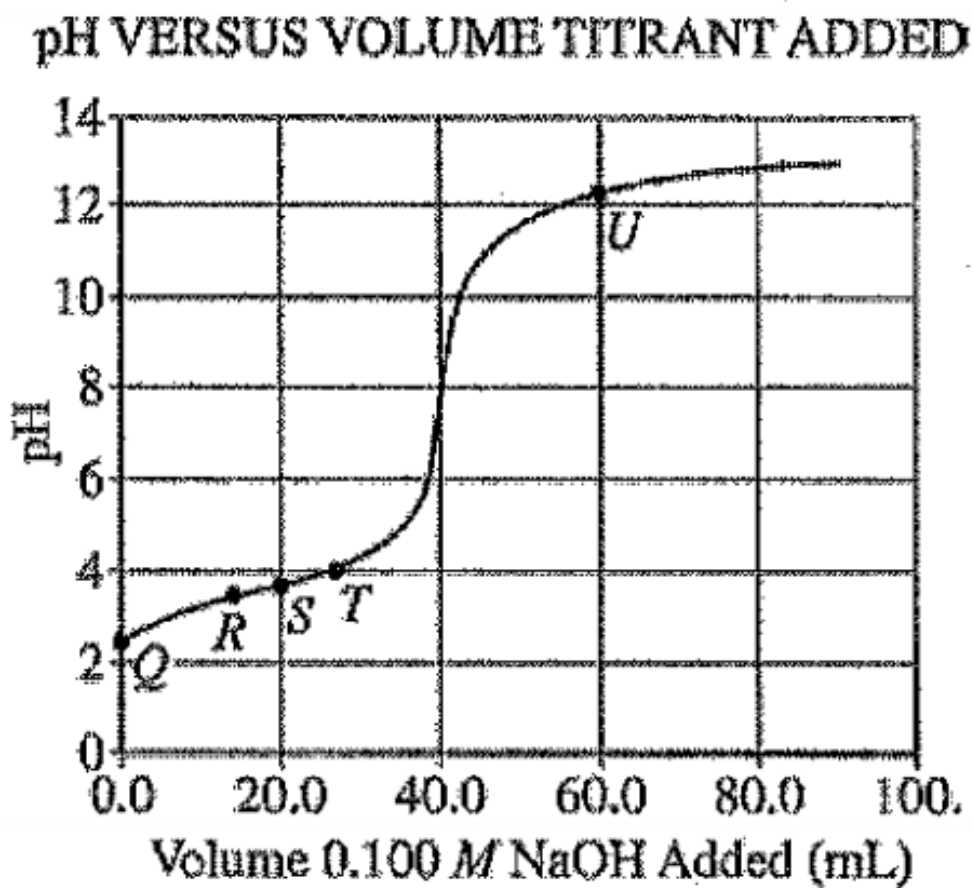


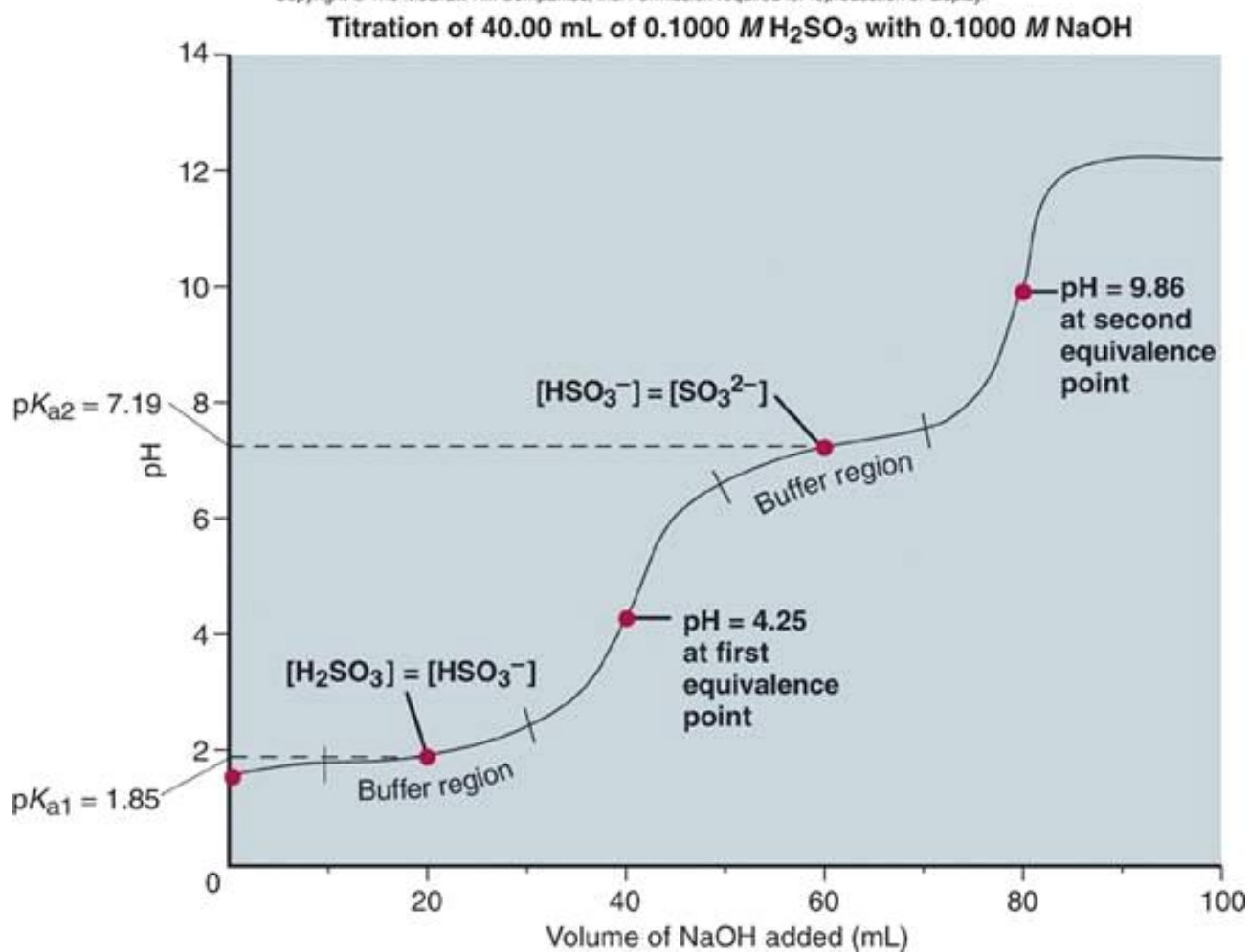
Sample Questions

Wednesday, April 5, 2017 12:32 PM

Question 4



- Equivalence occurs at 40.0 ml titrant added. So half equivalence at 20.0 ml of titrant.
- At half equivalence, $[HA] = [A^-]$. Below half equivalence, more acid species present.



Question 8

Kinetic Temperature

The expression for [gas pressure](#) developed from [kinetic theory](#) relates pressure and volume to the average molecular [kinetic energy](#). Comparison with the [ideal gas law](#) leads to an expression for [temperature](#) sometimes referred to as the kinetic temperature.

$$PV = nRT \longleftrightarrow PV = \frac{2}{3} N \left[\overline{\frac{1}{2} m v^2} \right]$$

This leads to the expression

$$T = \frac{2}{3} \frac{N}{nR} \left[\overline{\frac{1}{2} m v^2} \right] = \frac{2}{3} \frac{1}{k} \left[\overline{\frac{1}{2} m v^2} \right]$$

where N is the number of molecules, n the number of moles, R the [gas constant](#), and k the [Boltzmann constant](#). The more familiar form expresses the average molecular kinetic energy:

$$KE_{avg} = \left[\overline{\frac{1}{2} m v^2} \right] = \frac{3}{2} kT$$

Show

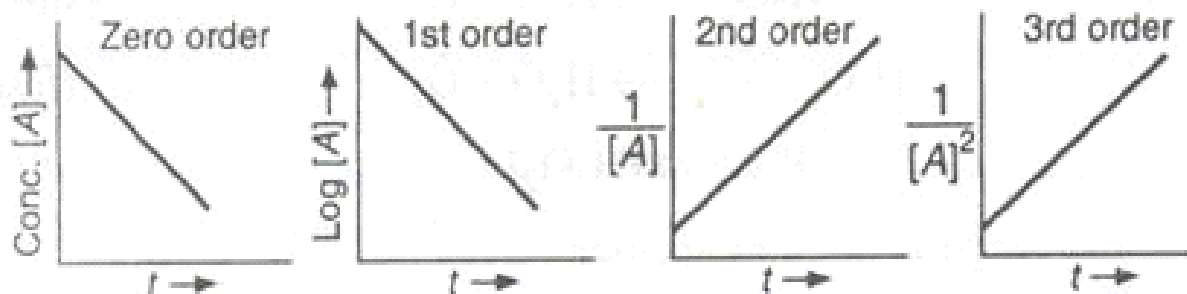
Question 19

Reactions can be '**driven by enthalpy**' (where a very exothermic **reaction** (negative ΔH) overcomes a decrease in **entropy**) or '**driven by entropy**' where an endothermic **reaction** occurs because of a highly positive ΔS . Example 1: The formation of $\text{NaCl}_{(s)}$ from its elements is spontaneous and releases a great deal of heat.

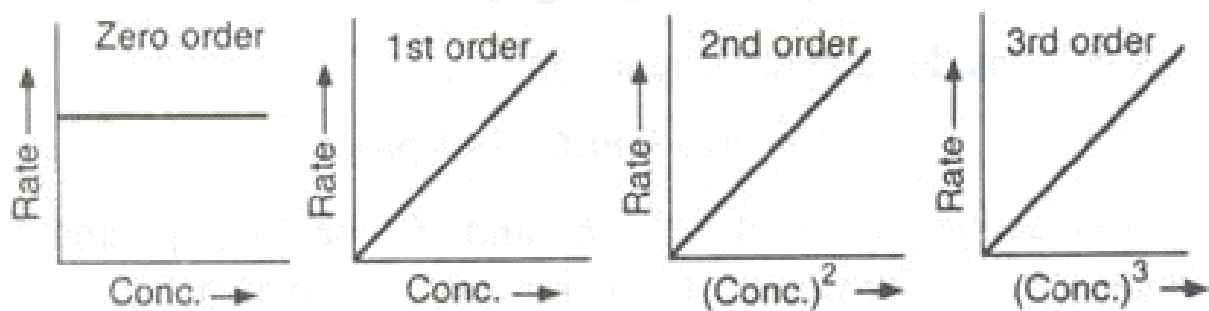
[Gibbs Free Energy - SoftSchools](#)

www.softschools.com/notes/ap_chemistry/gibbs_free_energy/

Question 26



(b) Plots from integrated rate equations:



Question 25

- Larger ionic radius --> smaller lattice energy --> lower boiling point

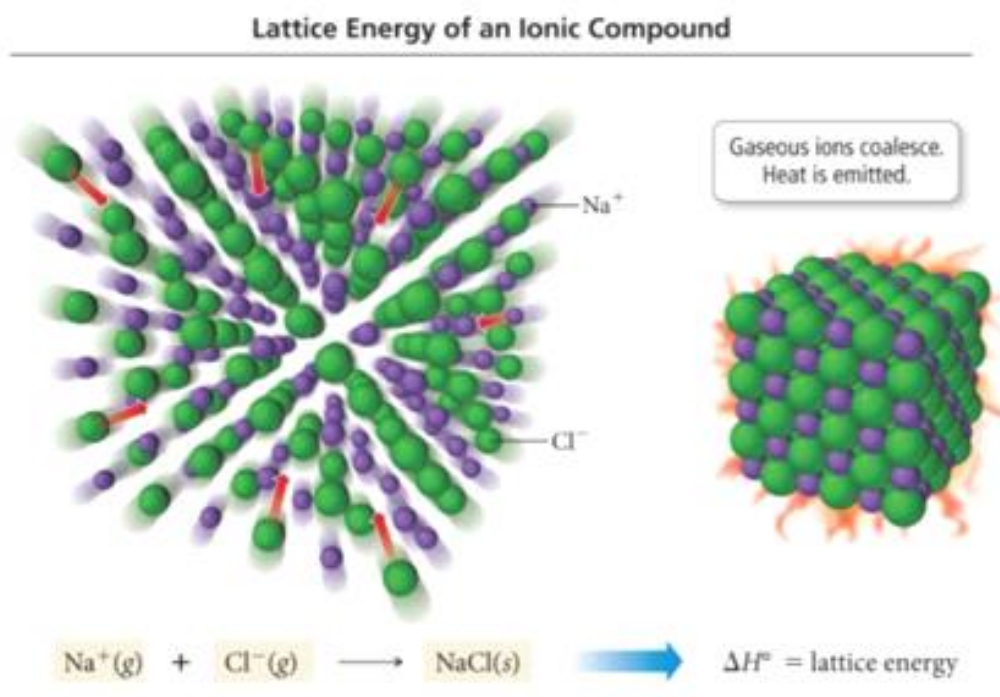
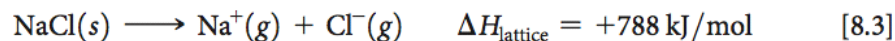
1999 Multiple Choice

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Question 4

The principal reason ionic compounds are stable is the attraction between ions of opposite charge. This attraction draws the ions together, releasing energy and causing the ions to form a solid array, or lattice, such as that shown in Figure 8.3. A measure of how much stabilization results from arranging oppositely charged ions in an ionic solid is given by the **lattice energy**, which is *the energy required to completely separate one mole of a solid ionic compound into its gaseous ions*.

To envision this process for NaCl, imagine that the structure in Figure 8.3 expands from within, so that the distances between the ions increase until the ions are very far apart. This process requires 788 kJ/mol, which is the value of the lattice energy:

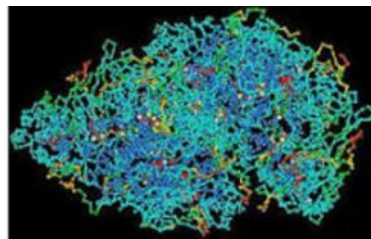


Question 9-12

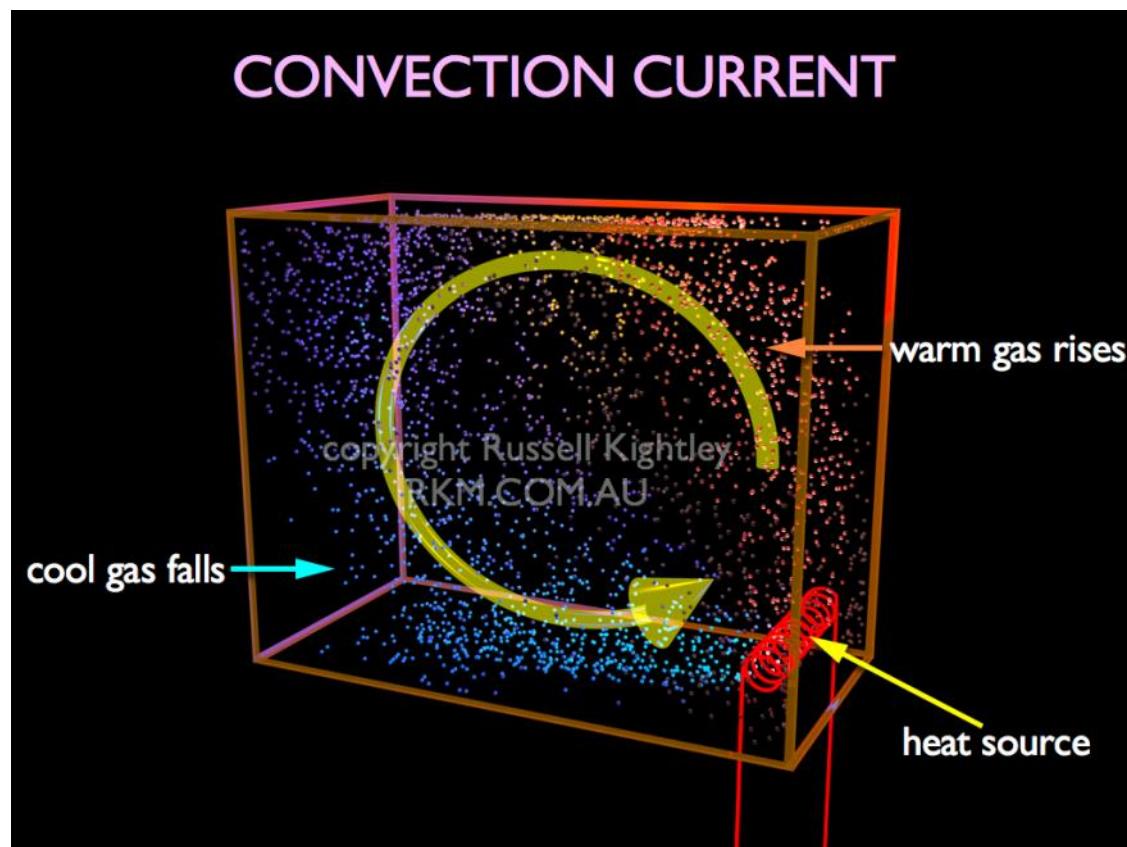
- Buffer
 - Weak Acid + Its Congregate Base
 - Weak Base + Its Congregate Acid

Question 13-16

A **macromolecule** is a very large molecule, such as protein, commonly created by polymerization of smaller subunits (monomers). They are typically composed of thousands of atoms or more.

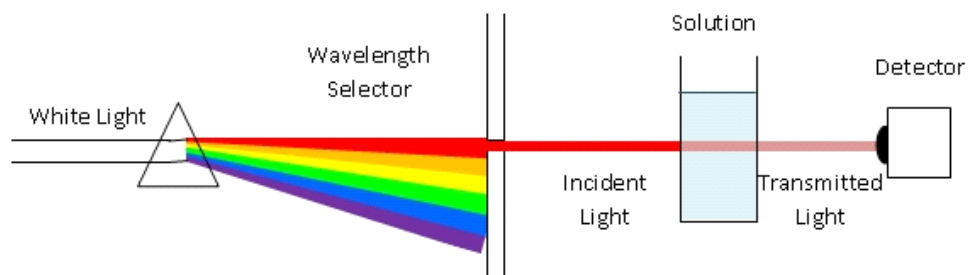


Question 23



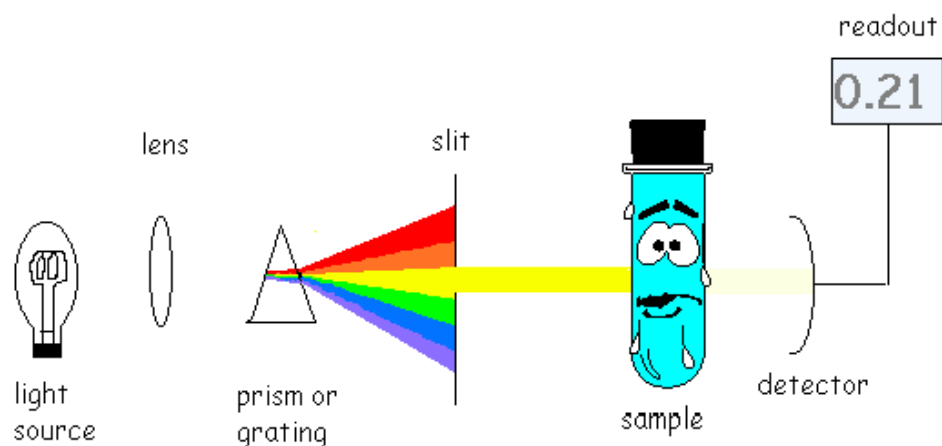
Question 27

- A visible-light **spectrophotometer** can determine the **concentration** of a solution



The difference between the incident and transmitted light indicates the absorbance

Spectrophotometer



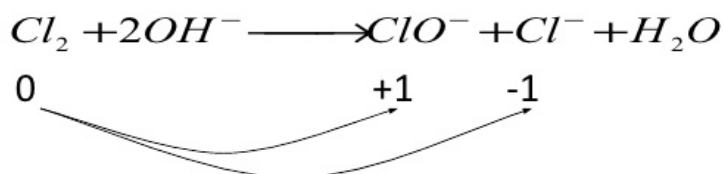
Question 30

Page 3

A Special Redox: Disproportionation

- Definition:

A disproportionation reaction is a redox reaction in which one species is **simultaneously** oxidised and reduced.



- Chlorine is simultaneously reduced from oxidation state of 0 in Cl₂ to -1 in Cl⁻, and oxidised from oxidation state of 0 in Cl₂ to +1 in ClO⁻.

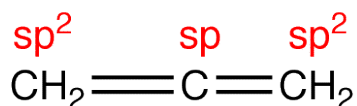
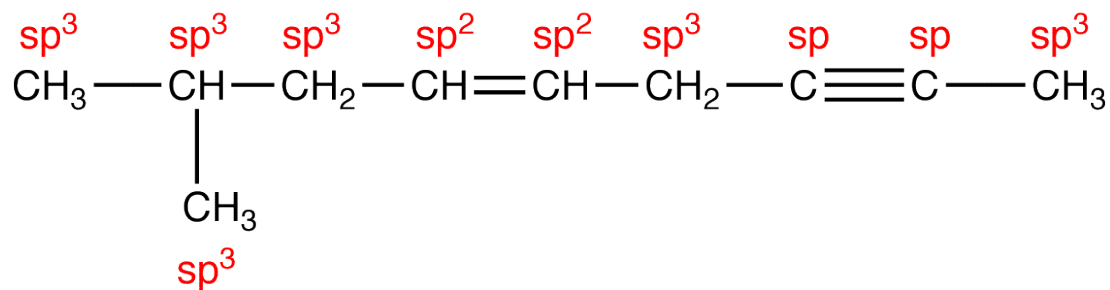
Question 31

$$\text{mole fraction, } X = \frac{\text{moles of solute}}{\text{moles of solution}}$$

$$\text{molarity, } M = \frac{\text{moles of solute}}{\text{liters of solution}}$$

$$\text{molality, } m = \frac{\text{moles of solute}}{\text{kg of solvent}}$$

Question 32



Question 35

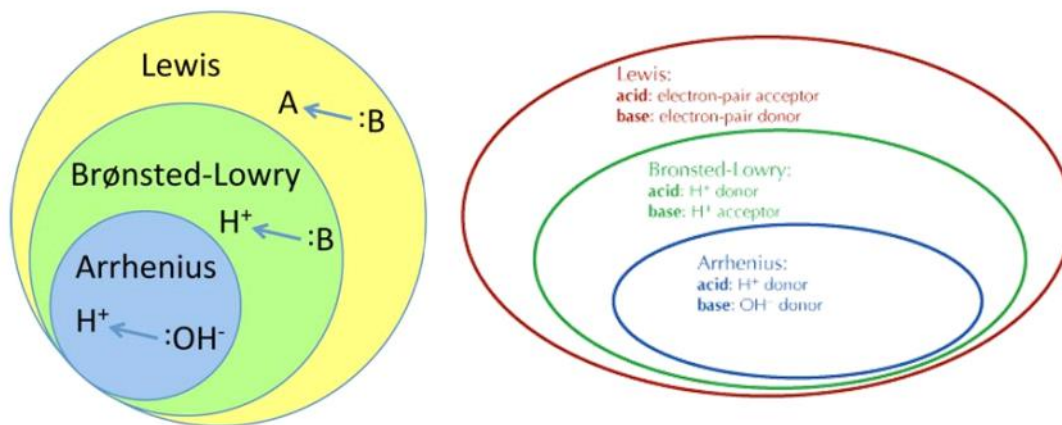
$$F = N_A \cdot Q_e$$

$$= 6.023 \cdot 10^{23} (\text{mol}^{-1}) \times 1.602 \times 10^{-19} (\text{C})$$

$$= 96485 \text{ C mol}^{-1}.$$

Question 38

Acid/Base Venn Diagram



All Brønsted-Lowry acids are Arrhenius acids.

Not all Arrhenius acids are Brønsted-Lowry acids.

etc...

60

Question 39

- The **normal melting point** of a solid is defined as the temperature at which the solid and liquid are in equilibrium at a total pressure of 1 atmosphere.

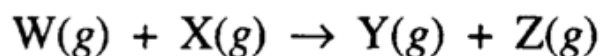
Question 43

- When **excess ammonia** is added to a solution of $\text{Cu}(\text{NO}_3)_2$, the color of blue will be **darker**.
- $\text{Cu}(\text{NO}_3)_2 + 4\text{NH}_3 = [\text{Cu}(\text{NH}_3)_4](\text{NO}_3)_2$

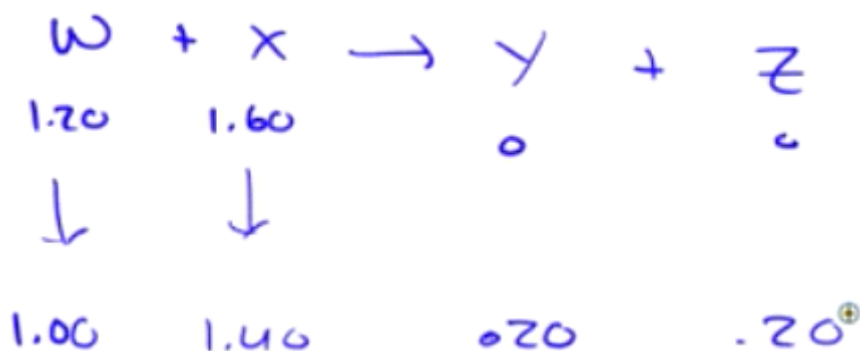


- Adding Ammonia To Copper II Nitrate.
- (left) Solution of blue $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (complex ion is $\text{Cu}(\text{H}_2\text{O})_6^{2+}$).
- (right) Addition of $\text{NH}_3(\text{aq})$ forms deep blue complex ion $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$.

Question 53



Gases W and X react in a closed, rigid vessel to form gases Y and Z according to the equation above. The initial pressure of $\text{W}(\text{g})$ is 1.20 atm and that of $\text{X}(\text{g})$ is 1.60 atm. No $\text{Y}(\text{g})$ or $\text{Z}(\text{g})$ is initially present. The experiment is carried out at constant temperature. What is the partial pressure of $\text{Z}(\text{g})$ when the partial pressure of $\text{W}(\text{g})$ has decreased to 1.0 atm?



Question 54

Keq

Only a temperature change can affect the value of Keq.

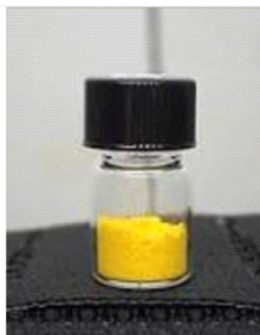
Changes in concentrations, pressure or surface area have **NO effect** on Keq.

- These changes correspond to increase in number of reacting molecules per liter.
- Increased once and then equilibrium is re-established.
- So ratios of products to reactants do not change.

Question 56

Lead(II) iodide

Chemical Compound



Lead(II) iodide or lead iodide is a salt with the formula PbI_2 . At room temperature, it is a bright yellow odorless crystalline solid, that becomes orange and red when heated. It was formerly called plumbous iodide.

[Wikipedia](#)

Formula: PbI_2

Molar mass: 461.01 g/mol

Density: 6.16 g/cm³

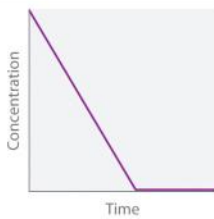
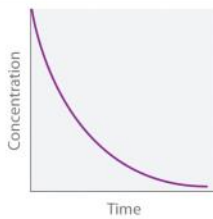
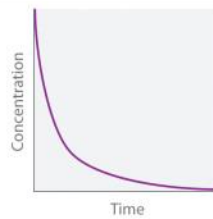
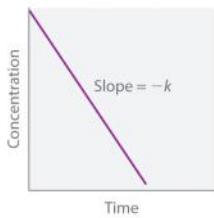

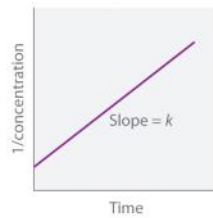
Boiling point: 872 °C

Appearance: bright yellow powder

Question 57

- The **standard reduction potential** is an **intrinsic** property. It will **not change** by the coefficient.

Question 63

	Zeroth Order	First Order	Second Order																								
Differential rate law	Rate = $-\frac{\Delta[A]}{\Delta t} = k$	Rate = $-\frac{\Delta[A]}{\Delta t} = k[A]$	Rate = $-\frac{\Delta[A]}{\Delta t} = k[A]^2$																								
Concentration vs. time																											
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$																								
Straight-line plot to determine rate constant																											
Relative rate vs. concentration	<table><tr><th>[A], M</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>1</td></tr><tr><td>3</td><td>1</td></tr></table>	[A], M	Rate, M/s	1	1	2	1	3	1	<table><tr><th>[A], M</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>2</td></tr><tr><td>3</td><td>3</td></tr></table>	[A], M	Rate, M/s	1	1	2	2	3	3	<table><tr><th>[A], M</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>4</td></tr><tr><td>3</td><td>9</td></tr></table>	[A], M	Rate, M/s	1	1	2	4	3	9
[A], M	Rate, M/s																										
1	1																										
2	1																										
3	1																										
[A], M	Rate, M/s																										
1	1																										
2	2																										
3	3																										
[A], M	Rate, M/s																										
1	1																										
2	4																										
3	9																										
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$																								
Units of k, rate constant	M/s	1/s	M ⁻¹ ·s ⁻¹																								

Question 54

What is the molar solubility in water of Ag_2CrO_4 ?

(The K_{sp} for Ag_2CrO_4 is 8×10^{-12} .)

$$K_{sp} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$$

$$(2x) \quad (x)$$

$$8 \times 10^{-12} = (2x)^2 (x) = 4x^2 \cdot x = 4x^3$$

$$x^3 = 2 \times 10^{-12}$$

$$x = \sqrt[3]{2 \times 10^{-12}}$$

Question 70

H_3PO_4 → С солями

$2\text{H}_3\text{PO}_4 + 3\text{AgNO}_3 = \text{Ag}_3\text{PO}_4 \downarrow + 3\text{HNO}_3$

Фосфорная
различными
Фосфорную
выпадению
раствором н

твовать с
делать по
действию с



$\text{H}_3\text{PO}_4 + 3\text{AgNO}_3 = \text{Ag}_3\text{PO}_4 \downarrow + 3\text{HNO}_3$

U

Question 72

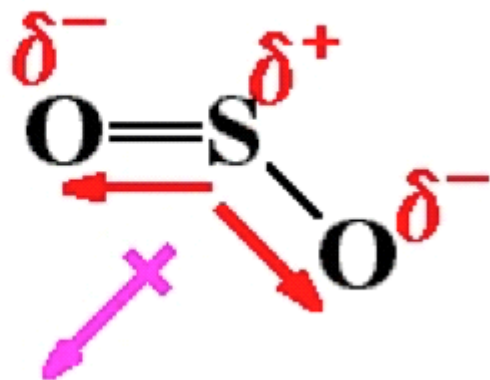
Crucible



originally used for metal, glass, and pigment production, a crucible is a container that can withstand temperatures high enough to melt or otherwise alter its contents

Question 74

- **SO₂** is a **polar** molecule, so it will **deviate** from **ideal** behavior.



1999 Free Response

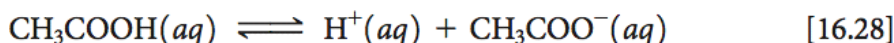
Sunday, April 2, 2017 9:19 PM

Question 1 (c)

Using K_a to Calculate pH

Knowing the value of K_a and the initial concentration of a weak acid, we can calculate the concentration of $H^+(aq)$ in a solution of the acid. Let's calculate the pH at 25 °C of a 0.30 M solution of acetic acid (CH_3COOH), the weak acid responsible for the characteristic odor and acidity of vinegar.

1. Our first step is to write the ionization equilibrium:

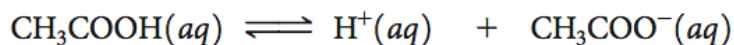


Notice that the hydrogen that ionizes is the one attached to an oxygen atom.

2. The second step is to write the equilibrium-constant expression and the value for the equilibrium constant. Taking $K_a = 1.8 \times 10^{-5}$ from Table 16.2, we write

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} \quad [16.29]$$

3. The third step is to express the concentrations involved in the equilibrium reaction. This can be done with a little accounting, as described in Sample Exercise 16.10. Because we want to find the equilibrium value for $[H^+]$, let's call this quantity x . The concentration of acetic acid before any of it ionizes is 0.30 M. The chemical equation tells us that for each molecule of CH_3COOH that ionizes, one $H^+(aq)$ and one $CH_3COO^-(aq)$ are formed. Consequently, if x moles per liter of $H^+(aq)$ form at equilibrium, x moles per liter of $CH_3COO^-(aq)$ must also form and x moles per liter of CH_3COOH must be ionized:



Initial concentration (M)	0.30	0	0
Change in concentration (M)	$-x$	$+x$	$+x$
Equilibrium concentration (M)	$(0.30 - x)$	x	x

4. The fourth step is to substitute the equilibrium concentrations into the equilibrium-constant expression and solve for x :

$$K_a = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{(x)(x)}{0.30 - x} = 1.8 \times 10^{-5} \quad [16.30]$$

This expression leads to a quadratic equation in x , which we can solve by using either an equation-solving calculator or the quadratic formula. We can simplify the problem, however, by noting that the value of K_a is quite small. As a result, we anticipate that the equilibrium lies far to the left and that x is much smaller than the initial concentration of acetic acid. Thus, we assume that x is negligible relative to 0.30, so that $0.30 - x$ is essentially equal to 0.30. We can (and should!) check the validity of this assumption when we finish the problem. By using this assumption, Equation 16.30 becomes

$$K_a = \frac{x^2}{0.30} = 1.8 \times 10^{-5}$$

Solving for x , we have

$$x^2 = (0.30)(1.8 \times 10^{-5}) = 5.4 \times 10^{-6}$$

$$x = \sqrt{5.4 \times 10^{-6}} = 2.3 \times 10^{-3}$$

$$[\text{H}^+] = x = 2.3 \times 10^{-3} M$$

$$\text{pH} = -\log(2.3 \times 10^{-3}) = 2.64$$

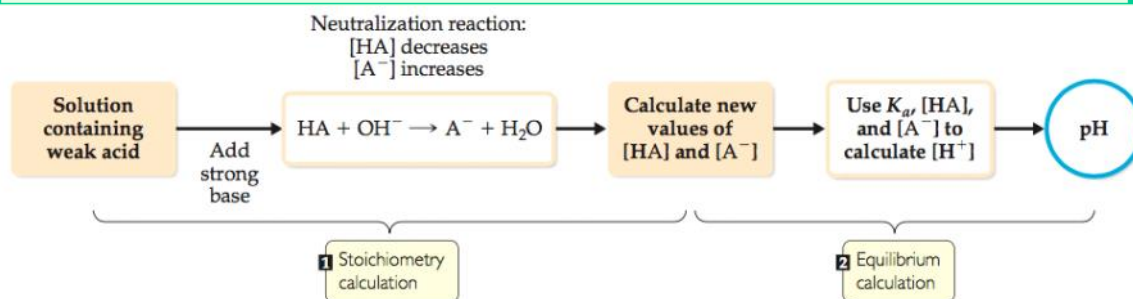
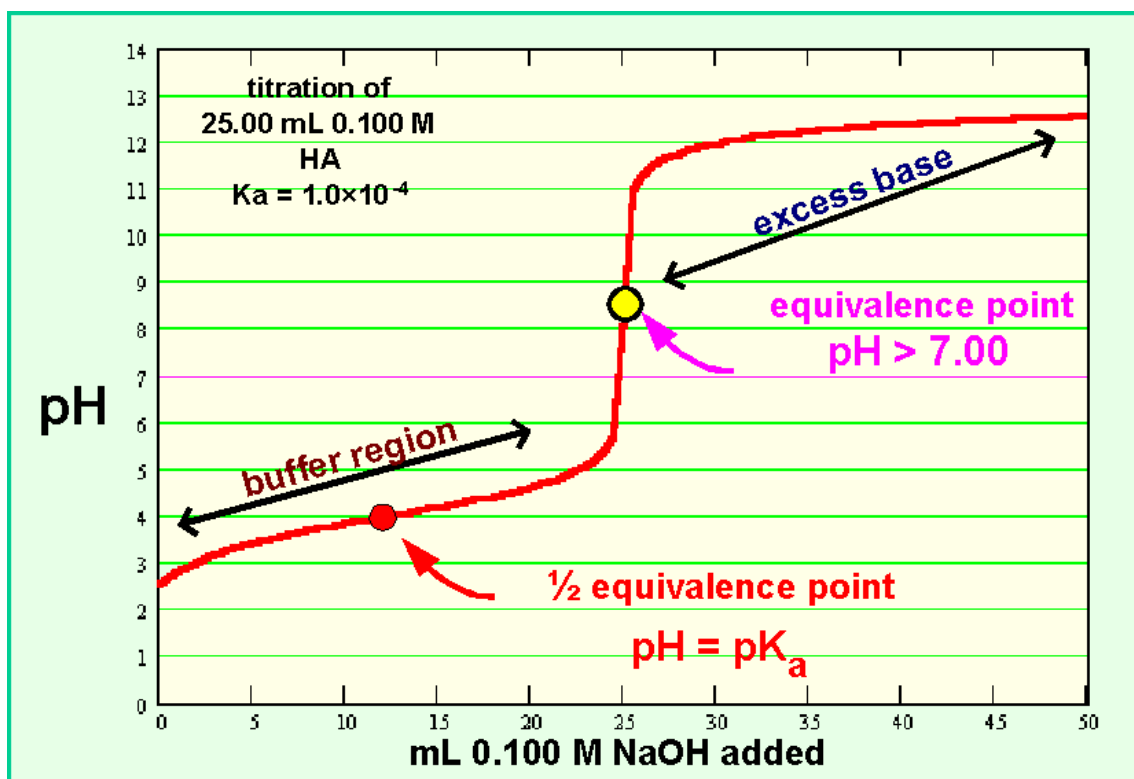
Now we check the validity of our simplifying assumption that $0.30 - x \approx 0.30$. The value of x we determined is so small that, for this number of significant figures, the assumption is entirely valid. We are thus satisfied that the assumption was a reasonable one to make. Because x represents the moles per liter of acetic acid that ionize, we see that, in this particular case, less than 1% of the acetic acid molecules ionize:

$$\text{Percent ionization of CH}_3\text{COOH} = \frac{0.0023 \text{ M}}{0.30 \text{ M}} \times 100\% = 0.77\%$$

As a general rule, if x is more than about 5% of the initial concentration value, it is better to use the quadratic formula. You should always check the validity of any simplifying assumptions after you have finished solving a problem.

We have also made one other assumption, namely that all of the H^+ in the solution comes from ionization of CH_3COOH . Are we justified in neglecting the autoionization of H_2O ? The answer is yes—the additional $[\text{H}^+]$ due to water, which would be on the order of 10^{-7} M , is negligible compared to the $[\text{H}^+]$ from the acid (which in this case is on the order of 10^{-3} M). In extremely precise work, or in cases involving very dilute solutions of acids, we would need to consider the autoionization of water more fully.

Question 1 (e)



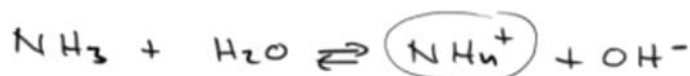
▲ Figure 17.10 Procedure for calculating pH when a weak acid is partially neutralized by a strong base.

ii) Stoichiometry 1st

$$15.0 \text{ mL} \times 0.0120 \frac{\text{mmol}}{\text{mL}} = 0.18 \text{ mmol } \text{H}^+$$

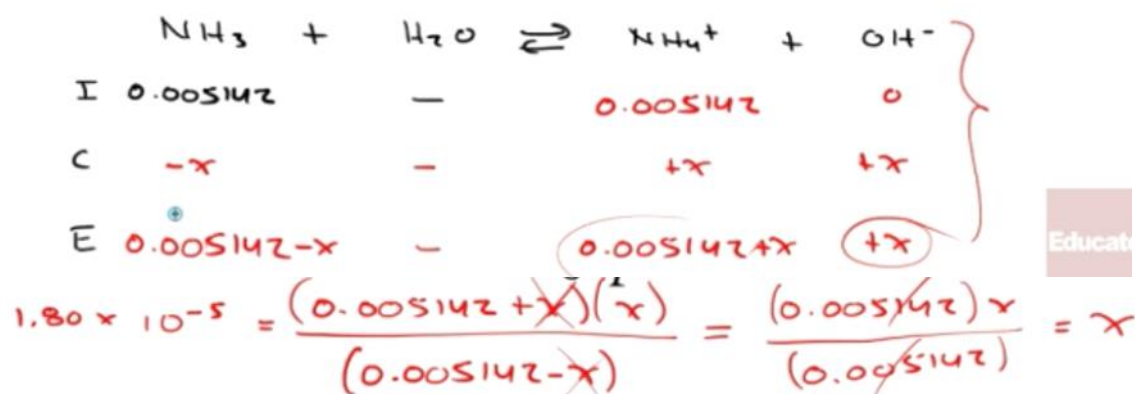
$$0.36 \text{ mmol } \text{NH}_3 - 0.18 \text{ mmol } \text{NH}_3 = 0.18 \text{ mmol } \text{NH}_3$$

Now we have $\frac{0.18 \text{ mmol } \text{NH}_3}{(20 + 15) \text{ mL}} = 0.005142 \text{ M}$



$$[\text{NH}_4^+] = 0.005142 \text{ M}$$

Equilibrium 2nd



$$x = [\text{OH}^-] = 1.80 \times 10^{-5}$$

$$\text{pOH} = 4.75$$

$$\text{pH} = 14.00 - 4.75 = 9.25$$

Question 2 (b)

$$E = h\nu = E_i - E_f = \frac{m_e q_e^4 (Z-1)^2}{8h^2 \epsilon_0^2} \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$$

or (dividing both sides by h to convert E to f):

$$f = \nu = \frac{m_e q_e^4}{8h^3 \epsilon_0^2} \left(\frac{3}{4} \right) (Z-1)^2 = (2.48 \cdot 10^{15} \text{ Hz})(Z-1)^2$$

$$\frac{1}{\lambda} = R(Z - \beta)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$\lambda \equiv$ Wavelength
 $R \equiv$ Rydberg constant
 $Z \equiv$ Atomic number
 $\beta \equiv$ Transition
 $n \equiv$ Integer : $n_1 < n_2$

The positive charge holding the electron is greater for He^+ , which has a 2+ nucleus, than for H with its 1+ nucleus. The stronger attraction means that it requires more energy **1 pt** for the electron to move to higher energy levels. Therefore, transitions from high energy states to lower states will be more energetic for He^+ than for H.

Note: Other arguments accepted, such as, “ E is proportional to Z^2 . Since $Z = 2$ for He^+ and $Z = 1$ for H, all energy levels in He^+ are raised (by a factor of 4).” Other accepted answers must refer to the increased charge on the He^+ nucleus, and NOT the mass.

Question 3 (b)

Reaction Orders: The Exponents in the Rate Law

The rate law for most reactions has the form

$$\text{Rate} = k[\text{reactant 1}]^m[\text{reactant 2}]^n \dots \quad [14.8]$$

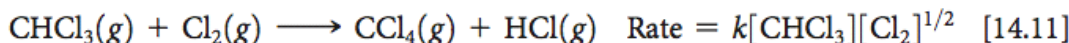
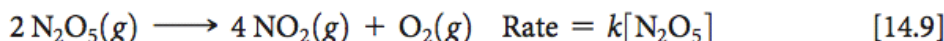
The exponents m and n are called **reaction orders**. For example, consider again the rate law for the reaction of NH_4^+ with NO_2^- :

$$\text{Rate} = k[\text{NH}_4^+][\text{NO}_2^-]$$

Because the exponent of $[\text{NH}_4^+]$ is 1, the rate is *first order* in NH_4^+ . The rate is also first order in NO_2^- . (The exponent 1 is not shown in rate laws.) The **overall reaction order** is the sum of the orders with respect to each reactant represented in the rate law. Thus, for the $\text{NH}_4^+ - \text{NO}_2^-$ reaction, the rate law has an overall reaction order of $1 + 1 = 2$, and the reaction is *second order overall*.

The exponents in a rate law indicate how the rate is affected by each reactant concentration. Because the rate at which NH_4^+ reacts with NO_2^- depends on $[\text{NH}_4^+]$ raised to the first power, the rate doubles when $[\text{NH}_4^+]$ doubles, triples when $[\text{NH}_4^+]$ triples, and so forth. Doubling or tripling $[\text{NO}_2^-]$ likewise doubles or triples the rate. If a rate law is second order with respect to a reactant, $[\text{A}]^2$, then doubling the concentration of that substance causes the reaction rate to quadruple because $[2]^2 = 4$, whereas tripling the concentration causes the rate to increase ninefold: $[3]^2 = 9$.

The following are some additional examples of experimentally determined rate laws:



Although the exponents in a rate law are sometimes the same as the coefficients in the balanced equation, this is not necessarily the case, as Equations 14.9 and 14.11 show. For any reaction, *the rate law must be determined experimentally*. In most rate laws, reaction orders are 0, 1, or 2. However, we also occasionally encounter rate laws in which the reaction order is fractional (as is the case with Equation 14.11) or even negative.

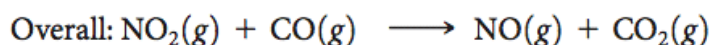
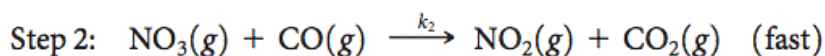
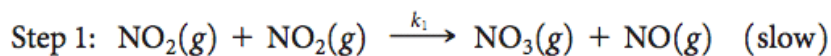
Table 14.3 Elementary Reactions and Their Rate Laws

Molecularity	Elementary Reaction	Rate Law
Unimolecular	$\text{A} \longrightarrow \text{products}$	$\text{Rate} = k[\text{A}]$
Bimolecular	$\text{A} + \text{A} \longrightarrow \text{products}$	$\text{Rate} = k[\text{A}]^2$
Bimolecular	$\text{A} + \text{B} \longrightarrow \text{products}$	$\text{Rate} = k[\text{A}][\text{B}]$
Termolecular	$\text{A} + \text{A} + \text{A} \longrightarrow \text{products}$	$\text{Rate} = k[\text{A}]^3$
Termolecular	$\text{A} + \text{A} + \text{B} \longrightarrow \text{products}$	$\text{Rate} = k[\text{A}]^2[\text{B}]$
Termolecular	$\text{A} + \text{B} + \text{C} \longrightarrow \text{products}$	$\text{Rate} = k[\text{A}][\text{B}][\text{C}]$

Question 3 (d)

Mechanisms with a Slow Initial Step

We can most easily see the relationship between the slow step in a mechanism and the rate law for the overall reaction by considering an example in which the first step in a multistep mechanism is the rate-determining step. Consider the reaction of NO_2 and CO to produce NO and CO_2 (Equation 14.23). Below 225°C , it is found experimentally that the rate law for this reaction is second order in NO_2 and zero order in CO : $\text{Rate} = k[\text{NO}_2]^2$. Can we propose a reaction mechanism consistent with this rate law? Consider the two-step mechanism:*



Step 2 is much faster than step 1; that is, $k_2 \gg k_1$, telling us that the intermediate $\text{NO}_3(g)$ is slowly produced in step 1 and immediately consumed in step 2.

Because step 1 is slow and step 2 is fast, step 1 is the rate-determining step. Thus, the rate of the overall reaction depends on the rate of step 1, and the rate law of the overall reaction equals the rate law of step 1. Step 1 is a bimolecular process that has the rate law

$$\text{Rate} = k_1[\text{NO}_2]^2$$

Thus, the rate law predicted by this mechanism agrees with the one observed experimentally. The reactant CO is absent from the rate law because it reacts in a step that follows the rate-determining step.

A scientist would not, at this point, say that we have “proved” that this mechanism is correct. All we can say is that the rate law predicted by the mechanism is *consistent with experiment*. We can often envision a different sequence of steps that leads to the same rate law. If, however, the predicted rate law of the proposed mechanism disagrees with experiment, we know for certain that the mechanism cannot be correct.

Question 5 (d)

$$\frac{|(\text{expt.} - \text{theor.})|}{\text{theor.}} \times 100$$

Question 6 (b)

- (b) (i) The reaction rate depends on the reaction kinetics, which is determined by the value of the activation energy, E_{act} . If the activation energy is large, a reaction that is thermodynamically spontaneous may proceed very slowly (if at all). **1 pt**

One point earned for linking the rate of the reaction to the activation energy, which may be explained verbally or shown on a reaction profile diagram

- (ii) The catalyst has no effect on the value of ΔG° .

1 pt

The catalyst reduces the value of E_{act} increasing the rate of reaction, but has no effect on the values of ΔH° and ΔS° , so it cannot affect the thermodynamics of the reaction.

1 pt

One point earned for indicating no change in the value of ΔG°

One point earned for indicating (verbally, or with a reaction-profile diagram) that the catalyst affects the activation energy

Question 7 (b)

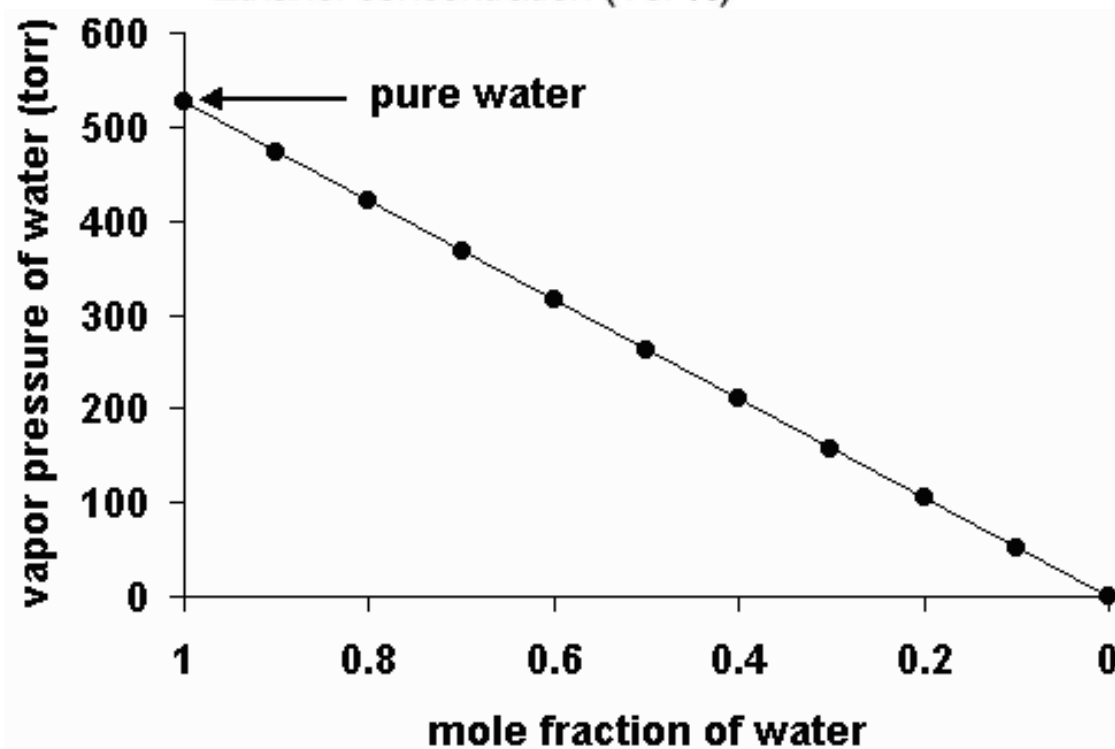
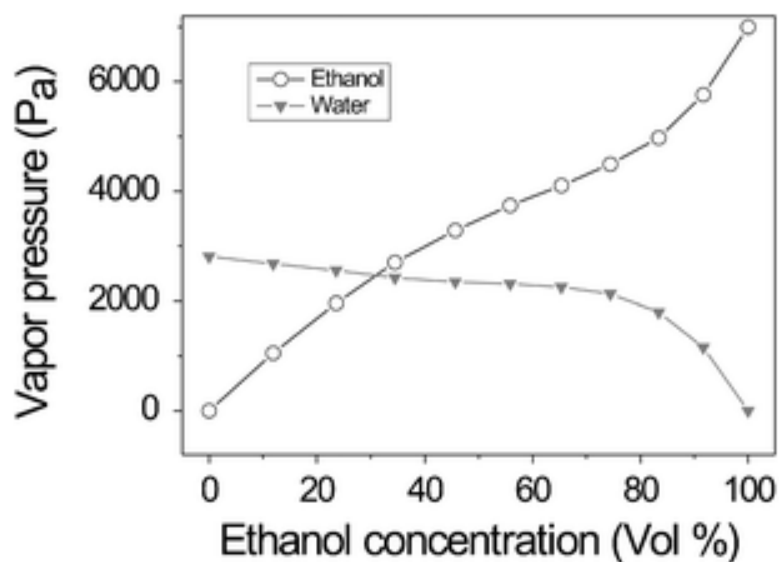
Expected and Observed Values of the van't Hoff Factor for 0.05 *m* Solutions of Several Electrolytes

Electrolyte	<i>i</i> (expected)	<i>i</i> (observed)
NaCl	2.0	1.9
MgCl ₂	3.0	2.7
MgSO ₄	2.0	1.3
FeCl ₃	4.0	3.4
HCl	2.0	1.9
Glucose*	1.0	1.0

*A nonelectrolyte shown for comparison.

Question 7 (c)

The lowering of vapor pressure of water is directly proportional to the concentration of solute particles in solution. C₂H₅OH is the only nonelectrolyte, so it will have the fewest solute particles in solution.



Question 7 (d)

These salts have a neutral cation and a basic anion. For example, **NaF** dissociates into Na^+ and F^- ions. The Na^+ ion has no acidic or basic properties, but the fluoride ion is a conjugate **base** of a **weak** acid and therefore is a basic anion. **NaF** a salt of the **NaOH**, a strong **base**, and **HF**, a **weak** acid.

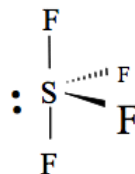
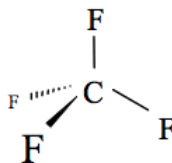
[hydrolysis and acid-base properties of salts \(15.10\)](http://www.mhhe.com/physsci/chemistry/chang7/ssg/chap15_10sg.html)

www.mhhe.com/physsci/chemistry/chang7/ssg/chap15_10sg.html

Question 8 (b)

(ii) CF_4 has a tetrahedral geometry, so the bond dipoles cancel, leading to a nonpolar molecule.

With five pairs of electrons around the central S atom, SF_4 exhibits a trigonal bipyramidal electronic geometry, with the lone pair of electrons. In this configuration, the bond dipoles do not cancel, and the molecule is polar.



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The **entropy** of a perfect crystal at absolute zero is exactly equal to zero. At absolute zero (zero kelvin), the system must be in a state with the minimum possible energy, and the above statement of the third law holds true provided that the perfect crystal has only one minimum energy state.

https://en.wikipedia.org/wiki/Third_law_of_thermodynamics

Rank the following compounds in order of increasing lattice energy: LiF, KBr, NaCl.



Remember the size of an ion INCREASES as you go down the periodic table.

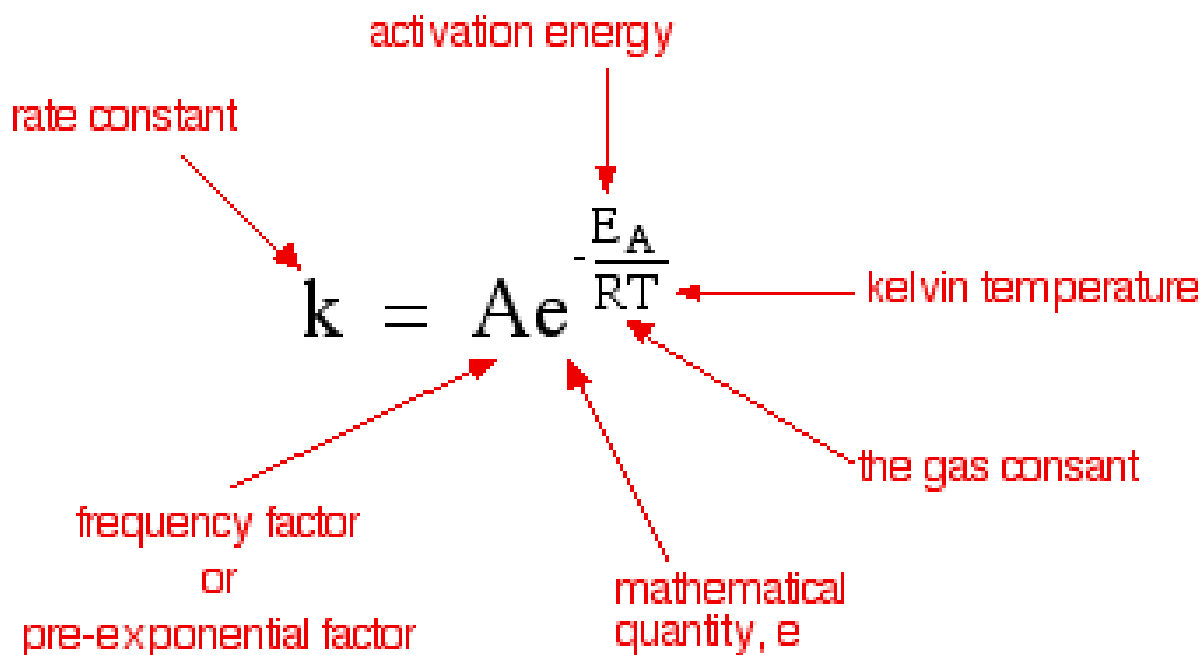
www.youtube.com

<https://www.boundless.com/chemistry/textbooks/...of.../lattice-energy-336-1485/>

- Quantity typically determined by measuring the rate of a reaction at two or more different temperatures: Activation Energy
- The activation energy can also be found algebraically by substituting two rate constants (k_1 , k_2) and the two corresponding reaction temperatures (T_1 , T_2) into the Arrhenius Equation

$$E_a = \frac{RT_1 T_2}{(T_1 - T_2)} \ln \frac{k_1}{k_2} \quad (6)$$

- Chemistry Page 26



Question 49

- Most Phosphates are insoluble

Many phosphates are not soluble in water at standard temperature and pressure. The sodium, **potassium**, rubidium, caesium, and **ammonium** phosphates are all water-soluble. Most other phosphates are only slightly soluble or are insoluble in water.

Phosphate - Wikipedia

<https://en.wikipedia.org/wiki/Phosphate>

Question 54

In chemistry, an **ideal solution** or **ideal** mixture is a **solution** with thermodynamic properties analogous to those of a mixture of **ideal** gases. ... The vapor pressure of the **solution** obeys Raoult's law, and the activity coefficient of each component (which measures deviation from ideality) is equal to one.

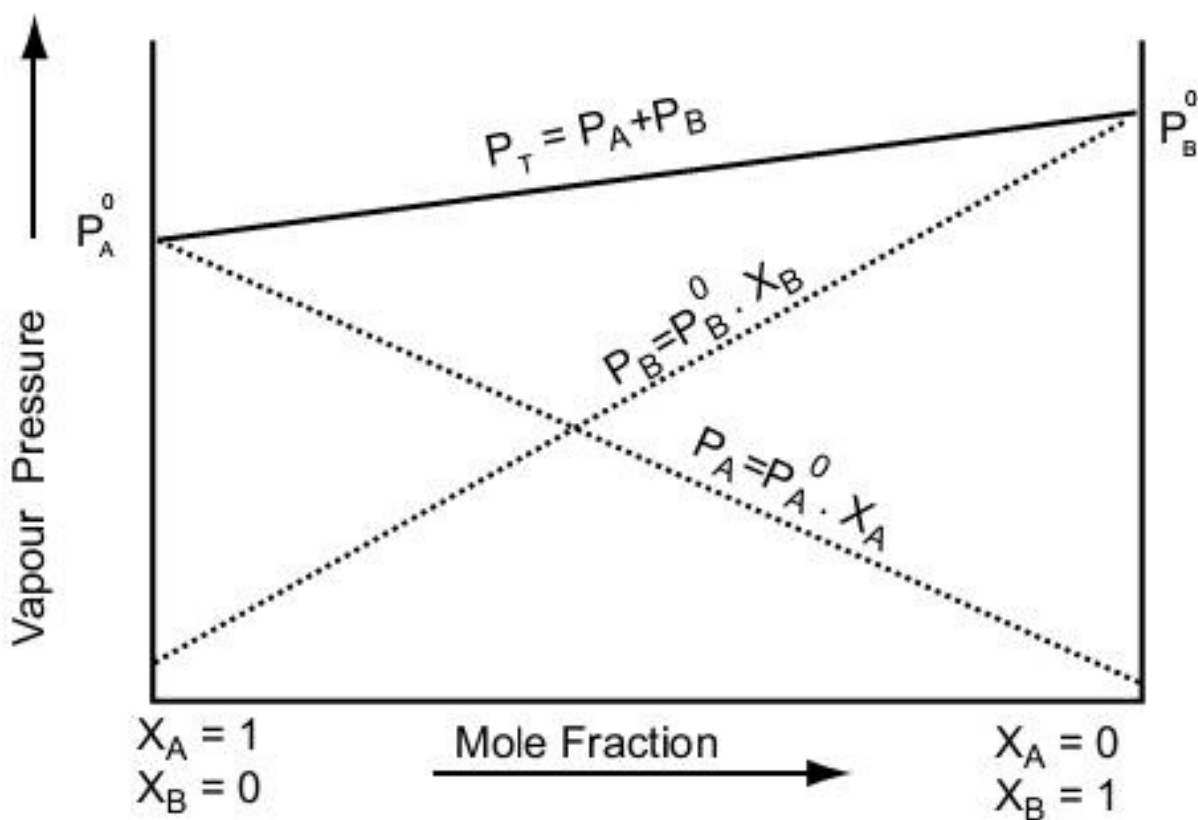
Ideal solution - Wikipedia

https://en.wikipedia.org/wiki/Ideal_solution

- Raoult's law

Raoult's Law

- The common mathematical statement for this behavior is known as Raoult's Law:
- $P_{\text{soln}} = X_{\text{solvent}} P_{\text{solvent}}$
- P_{soln} is the observed vapor pressure of the solution
- X_{solvent} is the mole fraction
- P_{solvent} is the vapor pressure of the pure solvent.



$$\chi_B = 0$$

$$\chi_B = 1$$

Vapour Pressure Diagram for Ideal Solution

Question 66

Factors that affect the rate of a chemical reaction include which of the following?

- I. Frequency of collisions of reactant particles
- II. Kinetic energy of collisions of reactant particles
- III. Orientation of reactant particles during collisions

- (A) II only
- (B) I and II only
- (C) I and III only
- (D) II and III only
- (E) I, II, and III**

- Collision Theory

Frequency Factor:
Number of Collisions per Second
Determined by the concentration of the reactants.

[Temperature has a smaller influence.]

Collision Theory

$$\text{Rate of Reaction} = \text{Number of Collisions per second} \times \times$$

↑
Frequency Factor

Energy Factor

Fraction of collisions with enough energy to react.

Determined by the Temperature

Collision Theory

$$\text{Rate of Reaction} = \text{Number of Collisions per second} \times \text{Fraction of collisions with enough energy to react} \times$$

↑
Energy Factor

Probability Factor

Fraction of collisions with
proper orientation

Determined by the shape of
the molecules

Collision Theory

$$\text{Rate of Reaction} = \text{Number of Collisions per second} \times \text{Fraction of collisions with enough energy to react} \times \text{Fraction of collisions with the proper orientation}$$

↑
Probability Factor

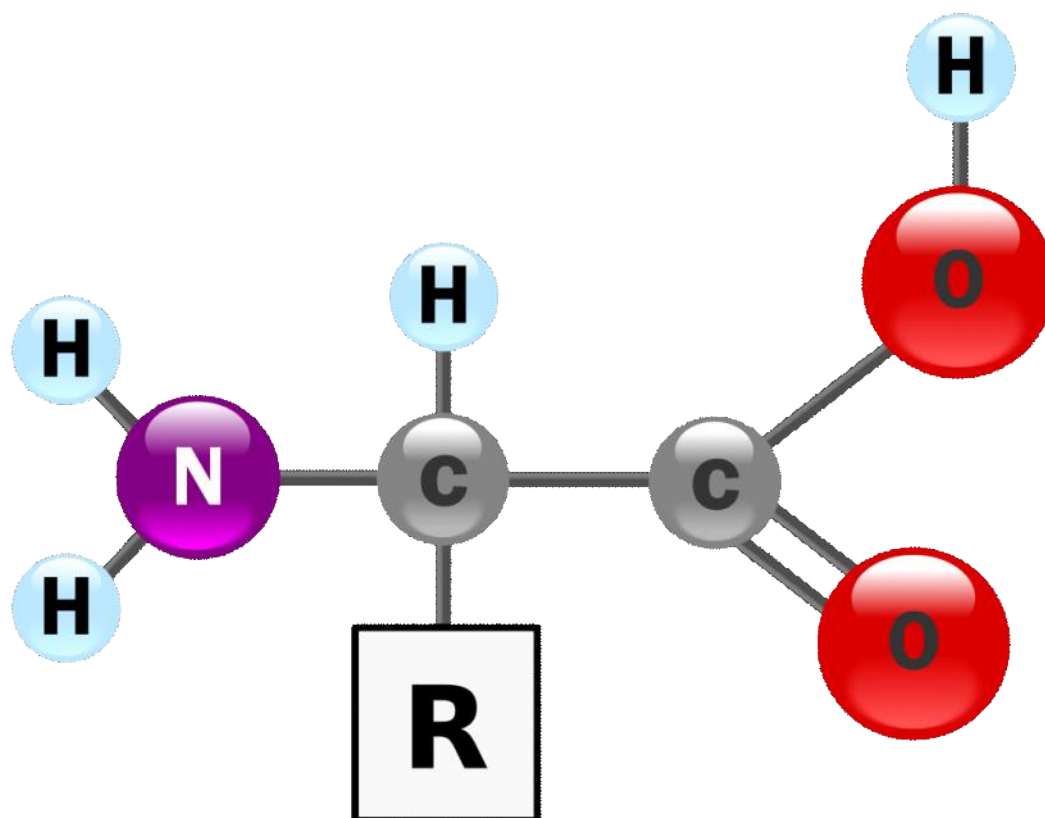
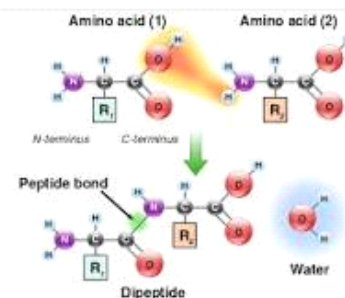
Question 70

Naturally produced amino acids typically contain all of the following elements EXCEPT

- (A) nitrogen
- (B) chlorine**
- (C) oxygen
- (D) hydrogen
- (E) carbon

The key elements of an amino acid are **carbon**, **hydrogen**, **oxygen**, and **nitrogen**, although other elements are found in the **side chains** of certain amino acids.

[Amino acid - Wikipedia](https://en.wikipedia.org/wiki/Amino_acid)
https://en.wikipedia.org/wiki/Amino_acid



2009 Multiple Choice

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Question 10

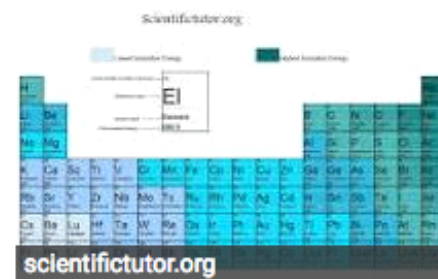
- Highest ionization energy: He

The first **ionization energy** varies in a predictable way across the periodic table. The **ionization energy** decreases from top to bottom in groups, and increases from left to right across a period. Thus, helium has the **largest** first **ionization energy**, while francium has one of the lowest.

Ionization Energy

https://www.angelo.edu/faculty/kboudrea/periodic/trends_ionization_energy.htm

You visited this page.



Question 11

- Ni^{2+} is light green

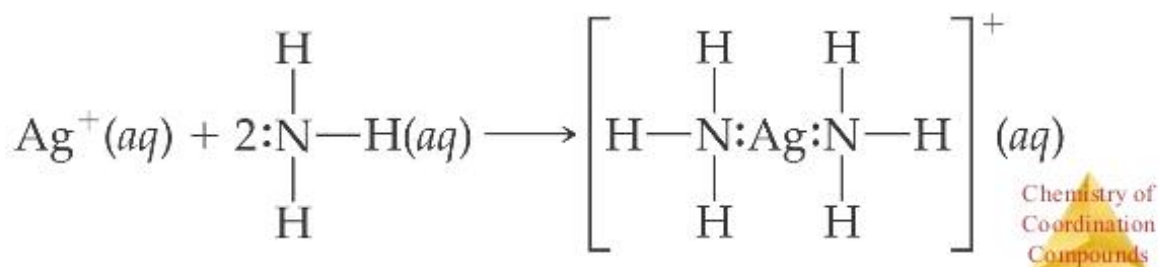


Question 15

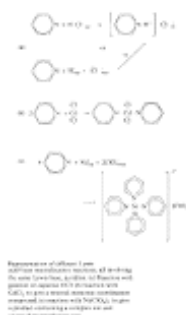
- Lewis acid-base reaction and coordination complex

Metal-Ligand Bond

- This bond is formed between a Lewis acid and a Lewis base.
 - The ligands (Lewis bases) have nonbonding electrons.
 - The metal (Lewis acid) has empty orbitals.

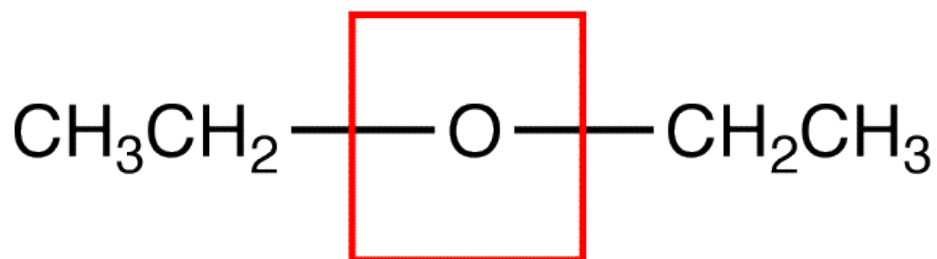


The **Lewis Acid-Base** Concept: **Coordination** Compounds. In a **Lewis acid-base** neutralization, the **base** donates a pair of electrons forming a **coordinate** covalent bond which joins the two species together into the reaction product.



The Lewis Acid Base Concept: Coordination Chemistry
<https://www.wou.edu/las/physci/ch412/ligand.htm>

Question 28

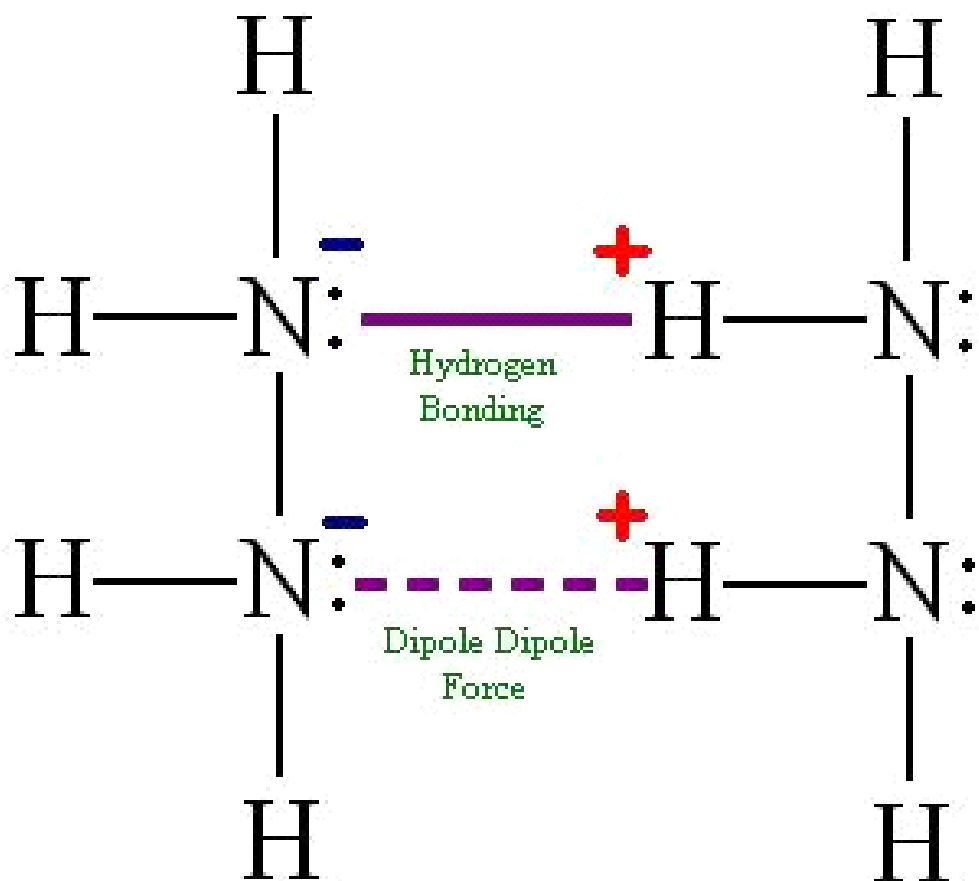


ether group

Esters	Ethers
General Formula:	General Formula:
$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{O}-\text{R}' \end{array}$	$\text{R}-\text{O}-\text{R}'$

Question 34

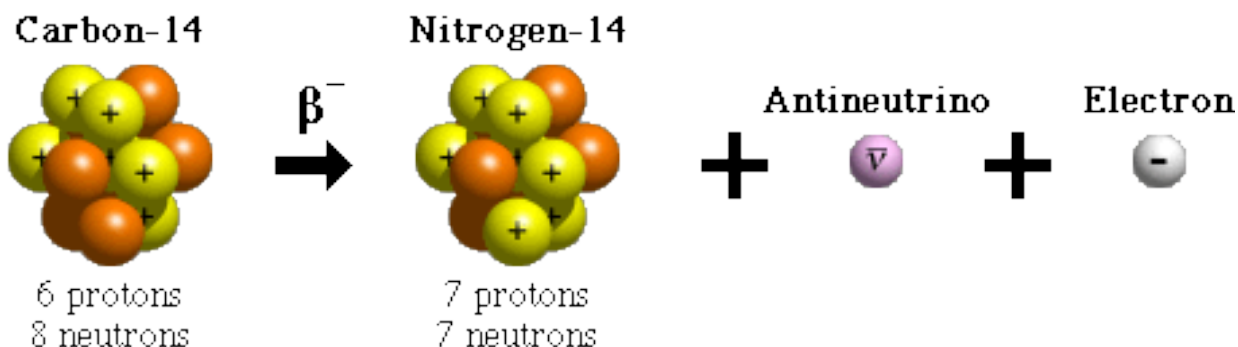
- Hydrogen bonding in N₂H₄



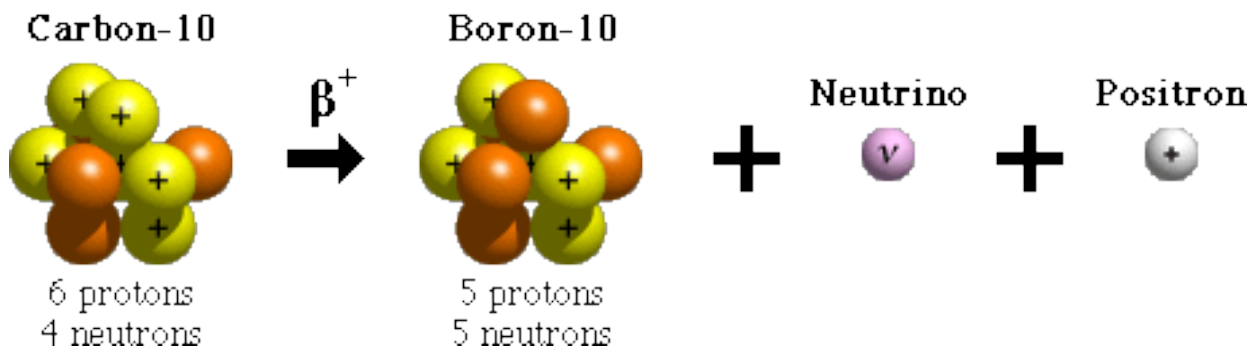
Question 40

- Beta plus decay vs. Beta minus decay

Beta-minus Decay



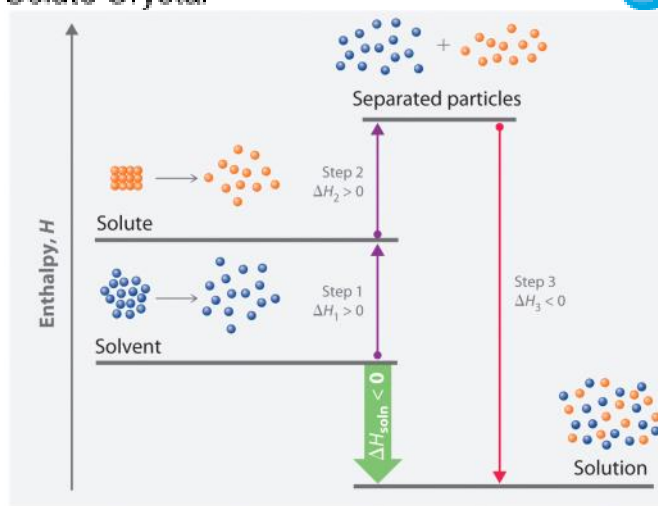
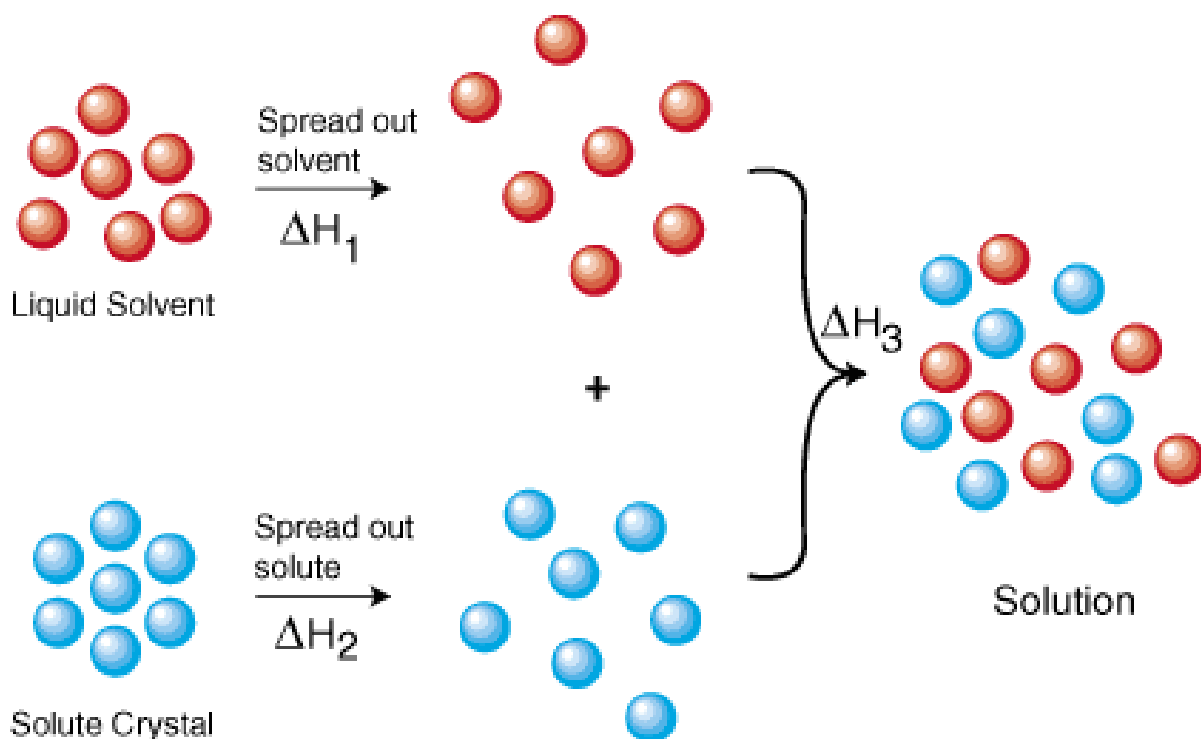
Beta-plus Decay



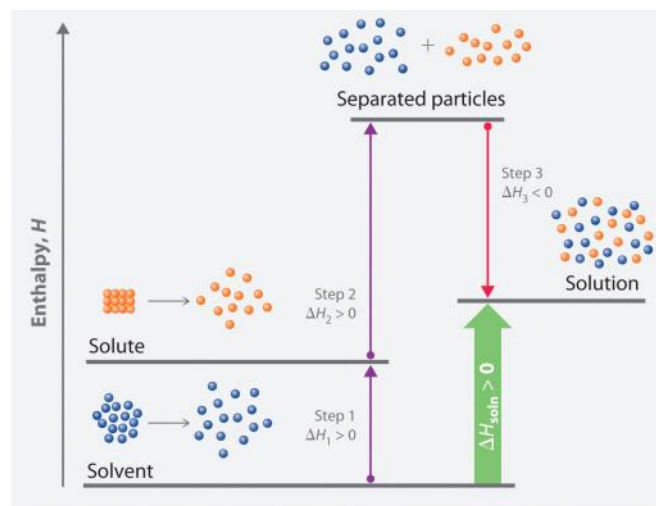
Question 71

When a solution is formed by adding some methanol, CH_3OH , to water, processes that are endothermic include which of the following?

- Methanol molecules move water molecules apart as the methanol goes into solution.
- Water molecules move methanol molecules apart as the methanol goes into solution.
- Intermolecular attractions form between molecules of water and methanol as the methanol goes into solution.



(a) Exothermic solution formation



(b) Endothermic solution formation

2009 Free Response

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Question 1 (a)

- HOI is a weaker acid than HOCl

(iii) Hypoiodous acid has the formula HOI. Predict whether HOI is a stronger acid or a weaker acid than the acid that you identified in part (a)(i). Justify your prediction in terms of chemical bonding.

HOI is a weaker acid than HOCl because the O–H bond in HOI is stronger than the O–H bond in HOCl. The lower electronegativity (electron-drawing ability) of I compared with that of Cl results in an electron density that is higher (hence a bond that is stronger) between the H and O atoms in HOI compared with the electron density between the H and O atoms in HOCl.

OR

The conjugate base OCl^- is more stable than OI^- because Cl, being more electronegative, is better able to accommodate the negative charge.

One point is earned for predicting that HOI is a weaker acid than HOCl and stating that iodine has a lower electronegativity than chlorine **and EITHER**

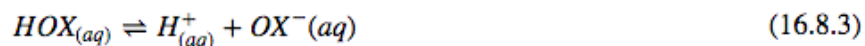
- stating that this results in a stronger O–H bond in HOI

OR

- stating that this decreases the stability of the OI^- ion in solution.

- Inductive Effects

Atoms or groups of atoms in a molecule other than those to which H is bonded can induce a change in the distribution of electrons within the molecule. This is called an inductive effect, and, much like the coordination of water to a metal ion, it can have a major effect on the acidity or basicity of the molecule. For example, the hypohalous acids (general formula HOX, with X representing a halogen) all have a hydrogen atom bonded to an oxygen atom. In aqueous solution, they all produce the following equilibrium:



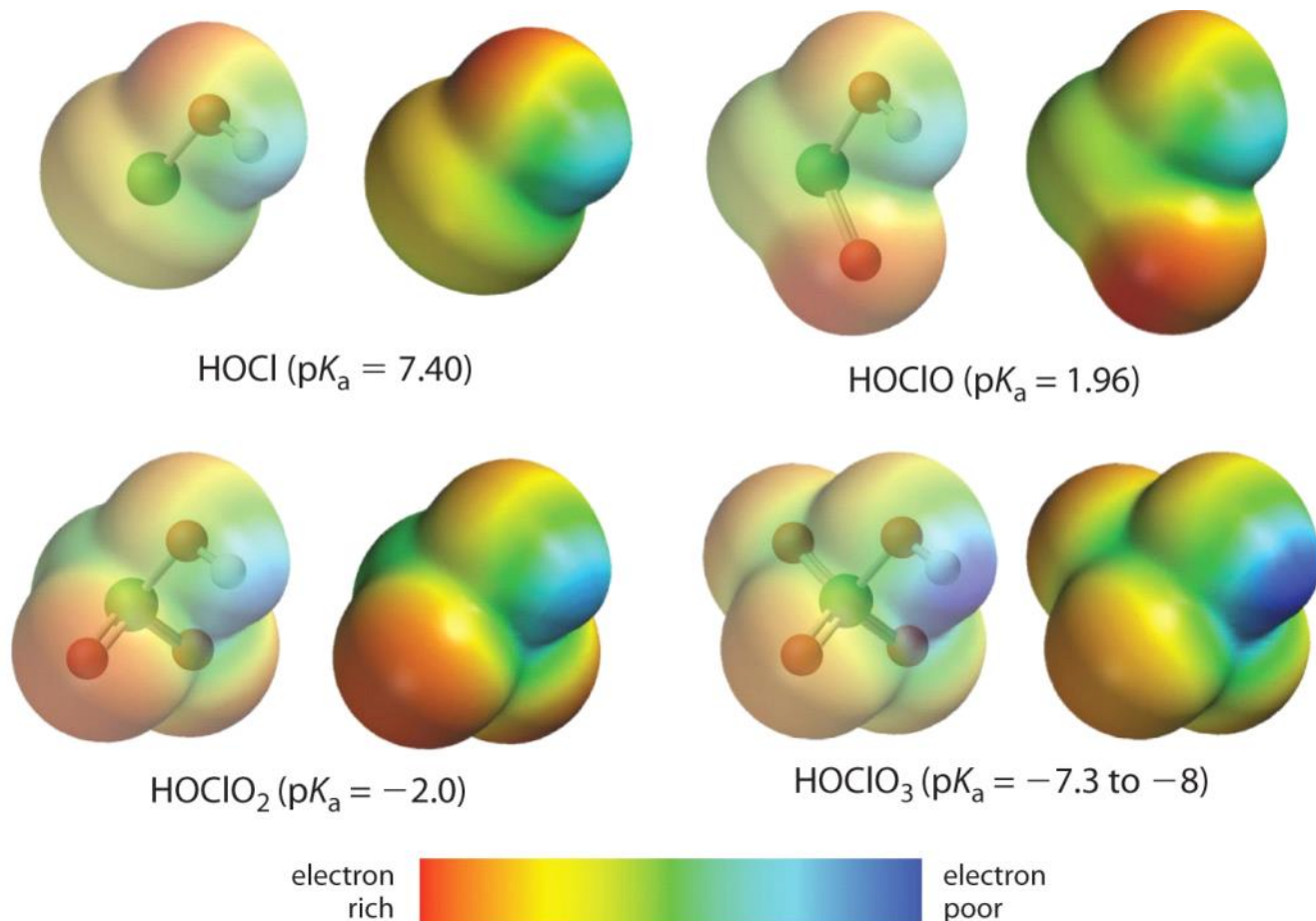
The acidities of these acids vary by about three orders of magnitude, however, due to the difference in electronegativity of the halogen atoms:

HOX	Electronegativity of X	pKa
HOCl	3.0	7.40
HOBr	2.8	8.55
HOI	2.5	10.5

As the electronegativity of X increases, the distribution of electron density within the molecule changes: the electrons are drawn more strongly toward the halogen atom and, in turn, away from the H in the O–H bond, thus weakening the O–H bond and allowing dissociation of hydrogen as H^{+} .

The acidity of oxoacids, with the general formula HOXO_n (with $n = 0\text{--}3$), depends strongly on the number of terminal oxygen atoms attached to the central atom X. As shown in Figure 16.8.1, the K_a values of the oxoacids of chlorine increase by a factor of about 10^4 to 10^6 with each oxygen as successive oxygen atoms are added. The increase in acid strength with increasing number of terminal oxygen atoms is due to both an inductive effect and increased stabilization of the conjugate base.

Because oxygen is the second most electronegative element, adding terminal oxygen atoms causes electrons to be drawn away from the O–H bond, making it weaker and thereby increasing the strength of the acid. The colors in Figure 16.8.1 show how the electrostatic potential, a measure of the strength of the interaction of a point charge at any place on the surface of the molecule, changes as the number of terminal oxygen atoms increases. In Figure 16.8.1 and Figure 16.8.2, blue corresponds to low electron densities, while red corresponds to high electron densities. The oxygen atom in the O–H unit becomes steadily less red from HClO to HClO_4 (also written as HOClO_3 , while the H atom becomes steadily bluer, indicating that the electron density on the O–H unit decreases as the number of terminal oxygen atoms increases. The decrease in electron density in the O–H bond weakens it, making it easier to lose hydrogen as H^{+} ions, thereby increasing the strength of the acid.



Question 2 (e)

- Percent error is always positive

Error = Experimental Value - Accepted Value

– Can be positive or **negative**

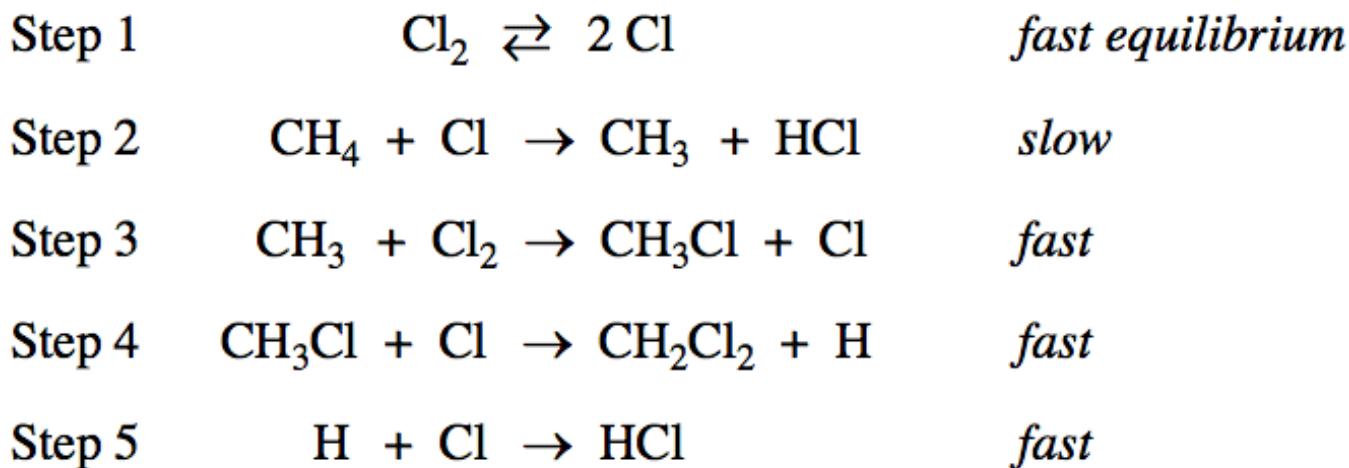
Percent Error = $\frac{|\text{error}|}{\text{accepted value}} \times 100\%$

– or

$$\% \text{ error} = \frac{|(\text{experimental value}) - (\text{known value})|}{\text{known value}}$$

– Always **positive**

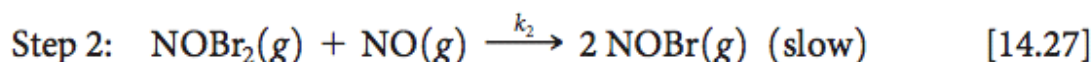
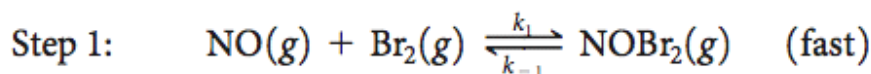
Question 3 (e)



<p>The order of the reaction with respect to Cl_2 is $\frac{1}{2}$.</p> <p>For step 1, $K = \frac{[\text{Cl}]^2}{[\text{Cl}_2]} \Rightarrow [\text{Cl}] = K^{1/2} [\text{Cl}_2]^{1/2}$</p> <p><u>Substituting into the rate law for step 2 (the slowest step in the mechanism):</u></p> $\text{rate} = k [\text{CH}_4] [\text{Cl}] = k [\text{CH}_4] (K^{1/2} [\text{Cl}_2]^{1/2})$ $= (k)(K^{1/2}) [\text{CH}_4] [\text{Cl}_2]^{1/2}$ <p>Because the exponent of Cl_2 in the rate law is $1/2$, the order of the reaction with respect to Cl_2 is $1/2$.</p>	<p>One point is earned for the correct answer with appropriate justification.</p>
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- Mechanisms with a Fast Initial Step

Let's consider an alternative mechanism that does not involve a termolecular step:



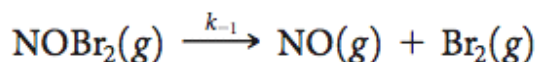
In this mechanism, step 1 involves two processes: a forward reaction and its reverse.

Because step 2 is the rate-determining step, the rate law for that step governs the rate of the overall reaction:

$$\text{Rate} = k_2[\text{NOBr}_2][\text{NO}] \quad [14.28]$$

Note that NOBr_2 is an intermediate generated in the forward reaction of step 1. Intermediates are usually unstable and have a low, unknown concentration. Thus, the rate law of Equation 14.28 depends on the unknown concentration of an intermediate, which isn't desirable. We want instead to express the rate law for a reaction in terms of the reactants, or the products if necessary, of the reaction.

With the aid of some assumptions, we can express the concentration of the intermediate NOBr_2 in terms of the concentrations of the starting reactants NO and Br_2 . We first assume that NOBr_2 is unstable and does not accumulate to any significant extent in the reaction mixture. Once formed, NOBr_2 can be consumed either by reacting with NO to form NOBr or by falling back apart into NO and Br_2 . The first of these possibilities is step 2 of our alternative mechanism, a slow process. The second is the reverse of step 1, a unimolecular process:



Because step 2 is slow, we assume that most of the NOBr_2 falls apart according to this reaction. Thus, we have both the forward and reverse reactions of step 1 occurring much faster than step 2. Because they occur rapidly relative to step 2, the forward and reverse reactions of step 1 establish an equilibrium. As in any other dynamic equilibrium, the rate of the forward reaction equals that of the reverse reaction:

$$\begin{array}{ccc} k[\text{NO}][\text{Br}_2] & = & k_{-1}[\text{NOBr}_2] \\ \text{Rate of forward reaction} & & \text{Rate of reverse reaction} \end{array}$$

Solving for $[\text{NOBr}_2]$, we have

$$[\text{NOBr}_2] = \frac{k_1}{k_{-1}} [\text{NO}][\text{Br}_2]$$

Substituting this relationship into Equation 14.28, we have

$$\text{Rate} = k_2 \frac{k_1}{k_{-1}} [\text{NO}][\text{Br}_2][\text{NO}] = k[\text{NO}]^2[\text{Br}_2]$$

where the experimental rate constant k equals $k_2 k_1 / k_{-1}$. This expression is consistent with the experimental rate law (Equation 14.25). Thus, our alternative mechanism (Equation 14.27), which involves two steps but only unimolecular and bimolecular processes, is far more probable than the single-step termolecular mechanism of Equation 14.26.

In general, *whenever a fast step precedes a slow one, we can solve for the concentration of an intermediate by assuming that an equilibrium is established in the fast step.*

Question 5 (d)

<p>The total bond energy of the reactants is larger.</p> <p>Reaction Y is <u>endothermic</u> ($\Delta H_{298}^\circ = +41 \text{ kJ mol}^{-1} > 0$), so there is a net input of energy as the reaction occurs. Thus, the total <u>energy required to break the bonds in the reactants must be greater than the total energy released when the bonds are formed in the products.</u></p>	<p>One point is earned for the correct answer with appropriate explanation.</p>
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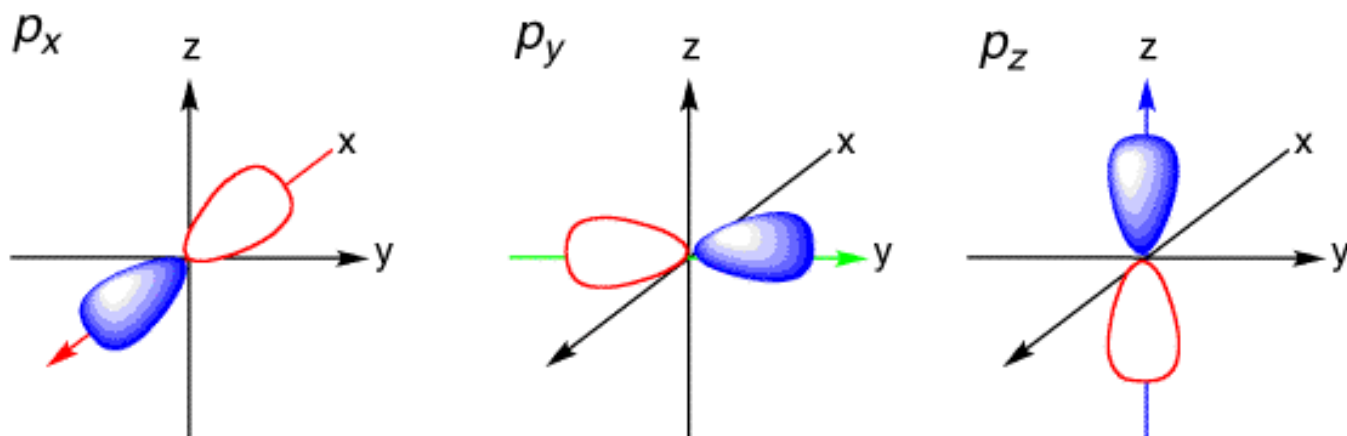
Question 5 (e)

- Thermodynamic data for an overall reaction have no bearing on how slowly or rapidly the reaction occurs

Question 6 (c)

- (c) In the H_2S molecule, the H–S–H bond angle is close to 90° . On the basis of this information, which atomic orbitals of the S atom are involved in bonding with the H atoms?

<p>The atomic orbitals involved in bonding with the H atoms in H_2S are p (specifically, $3p$) orbitals. The three p orbitals are mutually perpendicular (i.e., at 90°) to one another.</p>	<p>One point is earned for the correct answer.</p>
---	--



The three p orbitals are aligned along perpendicular axes

Question 6 (d)

- (ii) Compare the strength of the dipole-dipole forces in liquid H_2S to the strength of the dipole-dipole forces in liquid H_2O . Explain.

The strength of the dipole-dipole forces in liquid H_2S is weaker than that of the dipole-dipole forces in liquid H_2O . The net dipole moment of the H_2S molecule is less than that of the H_2O molecule. This results from the lesser polarity of the $\text{H}-\text{S}$ bond compared with that of the $\text{H}-\text{O}$ bond (S is less electronegative than O).

One point is earned for the correct answer with a correct explanation.

- Electronegativity and dipole-dipole force

Permanent Dipoles

- These occur when a two atoms sharing a covalent bond have substantially different electronegativity.
- HCl has a permanent dipole as Cl has a much higher electronegativity than H .
- Molecules with a permanent dipole are described as ***polar molecules***.

2009 Free Response (Form B)

2017年4月30日 星期日 下午1:18

Question 1 (c)

Of $\text{C}_2\text{H}_5\text{NH}_2(aq)$ and $\text{C}_2\text{H}_5\text{NH}_3^+(aq)$, which is present in the solution at the higher concentration at equilibrium? Justify your answer.

$\text{C}_2\text{H}_5\text{NH}_2$ is present in the solution at the higher concentration at equilibrium. Ethylamine is a weak base, and thus it has a small K_b value. Therefore only partial dissociation of $\text{C}_2\text{H}_5\text{NH}_2$ occurs in water, and $[\text{C}_2\text{H}_5\text{NH}_3^+]$ is thus less than $[\text{C}_2\text{H}_5\text{NH}_2]$.

One point is earned for the correct answer with justification.

Question 5 (c)

Given that ΔH_{298}° for the reaction is $-92.2 \text{ kJ mol}^{-1}$, which is larger, the total bond dissociation energy of the reactants or the total bond dissociation energy of the products? Explain.

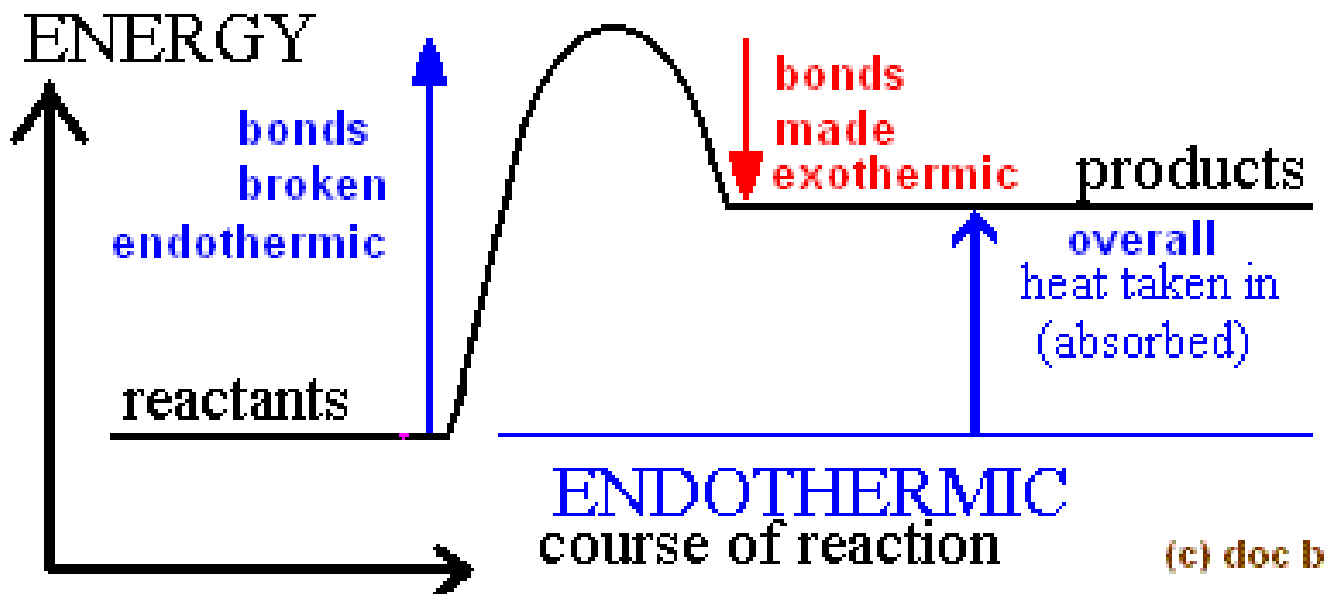
$$\Delta H_{298}^\circ = \Sigma (\text{bond energy of the reactants}) - \Sigma (\text{bond energy of the products})$$

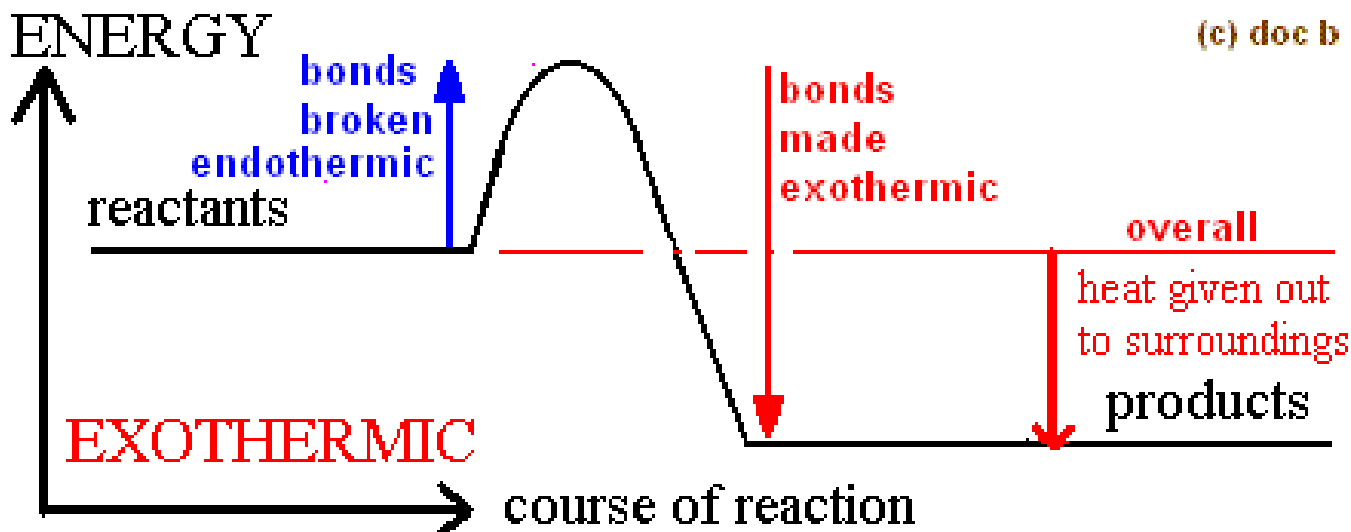
Based on the equation above, for ΔH_{298}° to be negative, the total bond energy of the products must be larger than the total bond energy of the reactants.

OR

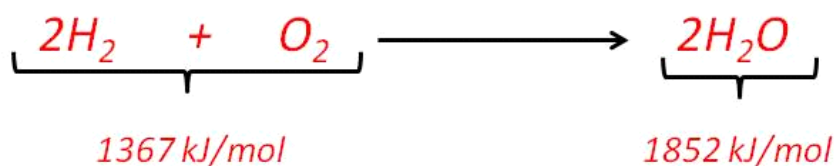
More energy is released as product bonds are formed than is absorbed as reactant bonds are broken.

One point is earned for the correct answer with the correct equation and explanation.





If we consider the reaction between hydrogen (H_2) and oxygen (O_2) to form water (H_2O), we see that the products have less energy than the reactants:



We know this because we can look up the bond energies of the different bonds that are breaking and forming, and add them up to find the total energy of both sides of the reaction:

$$\begin{array}{rcl}
 \begin{array}{l} \text{H-H} = 436 \text{ kJ/mol} \\ \text{x2 molecules of H}_2 \\ \hline 872 \text{ kJ/mol total energy} \end{array} & + & \begin{array}{l} \text{O=O} = 495 \text{ kJ/mol} \\ \text{x1 molecules of O}_2 \\ \hline 495 \text{ kJ/mol total energy} \end{array} = 1367 \text{ kJ/mol}
 \end{array}$$

$$\begin{array}{rcl}
 \begin{array}{l} \text{H-O} = 463 \text{ kJ/mol} \\ \text{x2 bonds per molecule of H}_2\text{O} \\ \hline 926 \text{ kJ/mol energy per molecule} \\ \text{formed} \end{array} & \times & \begin{array}{l} 2 \text{ molecules formed in} \\ \text{the reaction} \end{array} = 1852 \text{ kJ/mol}
 \end{array}$$

Because the formation of the products releases more energy (1852 kJ/mol) than the energy required to break the bonds of the reactants (1367 kJ/mol), this reaction is exothermic.

Question 5 (e)

- (i) Explain why there is a temperature above 298 K at which the algebraic sign of the value of ΔG° changes.

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

As the temperature increases $|T\Delta S^\circ|$ will at some point exceed $|\Delta H^\circ|$. Because both ΔH° and ΔS° are negative, the sign of ΔG° will then change from negative to positive.

One point is earned for the correct explanation.

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Question 1 (c)

- (c) A 50.0 mL sample of distilled water is added to the solution described in part (b), which is in a beaker with some solid AgBr at the bottom. The solution is stirred and equilibrium is reestablished. Some solid AgBr remains in the beaker. Is the value of $[Ag^+]$ greater than, less than, or equal to the value you calculated in part (b) ? Justify your answer.

The value of $[Ag^+]$ after addition of distilled water is equal to the value in part (b). The concentration of ions in solution in equilibrium with a solid does not depend on the volume of the solution.

One point is earned for the correct answer with justification.

Question 1 (e)

- (e) A student mixes 10.0 mL of $1.5 \times 10^{-4} M$ AgNO₃ with 2.0 mL of $5.0 \times 10^{-4} M$ NaBr and stirs the resulting mixture. What will the student observe? Justify your answer with calculations.

$$\begin{aligned}[Ag^+] &= \frac{(10.0 \text{ mL})(1.5 \times 10^{-4} M)}{12.0 \text{ mL}} = 1.3 \times 10^{-4} M \\[Br^-] &= \frac{(2.0 \text{ mL})(5.0 \times 10^{-4} M)}{12.0 \text{ mL}} = 8.3 \times 10^{-5} M \\Q &= [Ag^+][Br^-] = (1.3 \times 10^{-4} M)(8.3 \times 10^{-5} M) = 1.1 \times 10^{-8} \\1.1 \times 10^{-8} &> 5.0 \times 10^{-13}, \therefore \text{a precipitate will form.}\end{aligned}$$

One point is earned for calculation of concentration of ions.

One point is earned for calculation of Q and conclusion based on comparison between Q and K_{sp} .

One point is earned for indicating the precipitation of AgBr.

17.6 | Precipitation and Separation of Ions

Equilibrium can be achieved starting with the substances on either side of a chemical equation. For example, the equilibrium that exists between $\text{BaSO}_4(s)$, $\text{Ba}^{2+}(aq)$, and $\text{SO}_4^{2-}(aq)$ (Equation 17.15), can be achieved either by starting with $\text{BaSO}_4(s)$ or by starting with solutions containing Ba^{2+} and SO_4^{2-} . If we mix, say, a BaCl_2 aqueous solution with a Na_2SO_4 aqueous solution, BaSO_4 might precipitate out. How can we predict whether a precipitate will form under various conditions?

Recall that we used the reaction quotient Q in Section 15.6 to determine the direction in which a reaction must proceed to reach equilibrium. The form of Q is the same as the equilibrium-constant expression for a reaction, but instead of only equilibrium concentrations, you can use whatever concentrations are being considered. The direction in which a reaction proceeds to reach equilibrium depends on the relationship between Q and K for the reaction. If $Q < K$, the product concentrations are too low and reactant concentrations are too high relative to the equilibrium concentrations, and so the reaction will proceed to the right (toward products) to achieve equilibrium. If $Q > K$, product concentrations are too high and reactant concentrations are too low, and so the reaction will proceed to the left to achieve equilibrium. If $Q = K$, the reaction is at equilibrium.

For solubility-product equilibria, the relationship between Q and K_{sp} is exactly like that for other equilibria. For K_{sp} reactions, products are always the soluble ions, and the reactant is always the solid.

Therefore, for solubility equilibria,

- If $Q = K_{sp}$, the system is at equilibrium, which means the solution is saturated; this is the highest concentration the solution can have without precipitating.
- If $Q < K_{sp}$, the reaction will proceed to the right, towards the soluble ions; no precipitate will form.
- If $Q > K_{sp}$, the reaction will proceed to the left, towards the solid; precipitate will form.

For the case of the barium sulfate solution, then we would calculate $Q = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$, and compare this quantity to the K_{sp} for barium sulfate.

SAMPLE

EXERCISE 17.16 Predicting Whether a Precipitate Forms

Does a precipitate form when 0.10 L of $8.0 \times 10^{-3} M \text{Pb}(\text{NO}_3)_2$ is added to 0.40 L of $5.0 \times 10^{-3} M \text{Na}_2\text{SO}_4$?

SOLUTION

Analyze The problem asks us to determine whether a precipitate forms when two salt solutions are combined.

Plan We should determine the concentrations of all ions just after the solutions are mixed and compare the value of Q with K_{sp} for any potentially insoluble product. The possible metathesis products are

PbSO_4 and NaNO_3 . Like all sodium salts NaNO_3 is soluble, but PbSO_4 has a K_{sp} of 6.3×10^{-7} (Appendix D) and will precipitate if the Pb^{2+} and SO_4^{2-} concentrations are high enough for Q to exceed K_{sp} .

Solve When the two solutions are mixed, the volume is $0.10 \text{ L} + 0.40 \text{ L} = 0.50 \text{ L}$. The number of moles of Pb^{2+} is $0.10 \text{ L of } 8.0 \times 10^{-3} \text{ mol/L}$

$/ 8.0 \times 10^{-3} \text{ mol/L}$

SAMPLE EXERCISE 17.16 Predicting Whether a Precipitate Forms

Does a precipitate form when 0.10 L of $8.0 \times 10^{-3} M \text{Pb}(\text{NO}_3)_2$ is added to 0.40 L of $5.0 \times 10^{-3} M \text{Na}_2\text{SO}_4$?

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Solve When the two solutions are mixed, the volume is $0.10 \text{ L} + 0.40 \text{ L} = 0.50 \text{ L}$. The number of moles of Pb^{2+} in 0.10 L of $8.0 \times 10^{-3} M \text{Pb}(\text{NO}_3)_2$ is

$$(0.10 \text{ L}) \left(\frac{8.0 \times 10^{-3} \text{ mol}}{\text{L}} \right) = 8.0 \times 10^{-4} \text{ mol}$$

The concentration of Pb^{2+} in the 0.50-L mixture is therefore

$$[\text{Pb}^{2+}] = \frac{8.0 \times 10^{-4} \text{ mol}}{0.50 \text{ L}} = 1.6 \times 10^{-3} M$$

The number of moles of SO_4^{2-} in 0.40 L of $5.0 \times 10^{-3} M \text{Na}_2\text{SO}_4$ is

$$(0.40 \text{ L}) \left(\frac{5.0 \times 10^{-3} \text{ mol}}{\text{L}} \right) = 2.0 \times 10^{-3} \text{ mol}$$

Therefore

$$[\text{SO}_4^{2-}] = \frac{2.0 \times 10^{-3} \text{ mol}}{0.50 \text{ L}} = 4.0 \times 10^{-3} M$$

and

$$Q = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = (1.6 \times 10^{-3})(4.0 \times 10^{-3}) = 6.4 \times 10^{-6}$$

Because $Q > K_{sp}$, PbSO_4 precipitates.

Question 5 (f)

- (f) Ethanol is completely soluble in water, whereas ethanethiol has limited solubility in water. Account for the difference in solubilities between the two compounds in terms of intermolecular forces.

Ethanol is able to form strong hydrogen bonds with water whereas ethanethiol does not have similar capability. The formation of hydrogen bonds increases the attraction between molecules of ethanol and molecules of water, making them more soluble in each other.

Note: The answer must clearly focus on the solute-solvent interaction. Just the mention of hydrogen bonding does not earn the point.

One point is earned for the correct explanation.

+ Influence of substituents on the solubility

- Polar groups such as -OH capable of hydrogen bonding with water molecules impart high solubility
- Non-polar groups such as -CH_3 and -Cl are hydrophobic and impart low solubility.
- Ionization of the substituent increases solubility, e.g. -COOH and -NH_2 are slightly hydrophilic whereas -COO^- and -NH_3^+ are very hydrophilic.

Substituent	Classification
-CH_3	Hydrophobic
$\text{-CH}_2\text{-}$	Hydrophobic
-Cl, -Br, -F	Hydrophobic
$\text{-N(CH}_3)_2$	Hydrophobic
-SCH_3	Hydrophobic
$\text{-OCH}_2\text{CH}_3$	Hydrophobic
-OCH_3	Slightly hydrophilic
-NO_2	Slightly hydrophilic
-CHO	Hydrophilic
-COOH	Slightly hydrophilic
-COO^-	Very hydrophilic
-NH_2	Hydrophilic
-NH_3^+	Very hydrophilic
-OH^+	Very hydrophilic

Question 6 (b)

(b) Which species, Zn or Zn^{2+} , has the greater ionization energy? Justify your answer.

Zn^{2+} has the greater ionization energy. The electron being removed from Zn^{2+} experiences a larger effective nuclear charge than the electron being removed from Zn because Zn^{2+} has two fewer electrons shielding the nucleus.

OR

It takes more energy to remove a negatively charged electron from a positive ion than from a neutral atom.

One point is earned for identifying Zn^{2+} with justification.

Question 6 (g)

- (g) If the concentration of $\text{Al}(\text{NO}_3)_3$ in the $\text{Al}(s)/\text{Al}^{3+}(aq)$ half-cell is lowered from 1.0 M to 0.01 M at 25°C , does the cell voltage increase, decrease, or remain the same? Justify your answer.

Lowering $[\text{Al}^{3+}]$ causes an increase in the cell voltage.

The value of Q will fall below 1.0 and the log term in the Nernst equation will become negative. This causes the value of E_{cell} to become more positive.

OR

A decrease in a product concentration will increase the spontaneity of the reaction, increasing the value of E_{cell} .

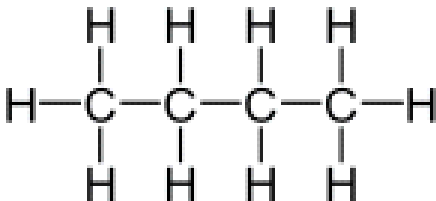
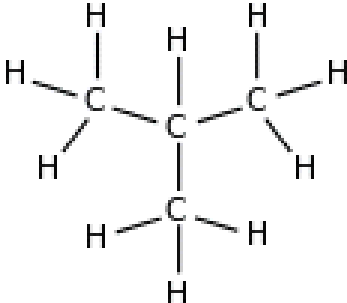

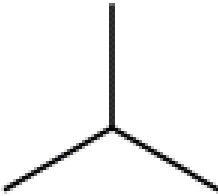
One point is earned for indicating that E_{cell} increases.

One point is earned for the correct justification.

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Question 1 (a)

Common name	normal butane unbranched butane <i>n</i>-butane	isobutane <i>i</i>-butane
IUPAC name	butane	2-methylpropane
Molecular diagram		
Skeletal diagram		

Question 1 (b)

- (b) On the basis of molecular structure, identify the isomer that has the higher boiling point. Justify your answer.

<p>The isomer <i>n</i>-butane has the higher boiling point. London (dispersion) forces are greater among molecules of <i>n</i>-butane than they are among molecules of isobutane because molecules of <i>n</i>-butane, with its <u>linear structure</u>, can approach one another <u>more closely</u> and can form a <u>greater number of induced temporary dipoles</u> than molecules of isobutane, with its more compact structure, can form.</p>	<p>One point is earned for the correct choice of isomer with justification.</p>
---	---

Question 2 (d)


- Log is 10-based in Chemistry

- (d) Calculate the value of the equilibrium constant, K_{eq} , for the cell reaction at 25°C. Explain what the magnitude of K_{eq} tells you about the extent of the reaction.

$\log K_{eq} = \frac{nE}{0.0592} = \frac{5 \times 0.72}{0.0592} = 61$ $K_{eq} = 6.5 \times 10^{60}$ <p>Because the magnitude of K_{eq} is very large, the extent of the cell reaction is also very large and the reaction goes essentially to completion.</p>	<p>One point is earned for the correct substitution.</p> <p>One point is earned for the correct numerical answer.</p> <p>One point is earned for an explanation.</p>
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Question 3 (d)

ore

/ôr/ 

noun

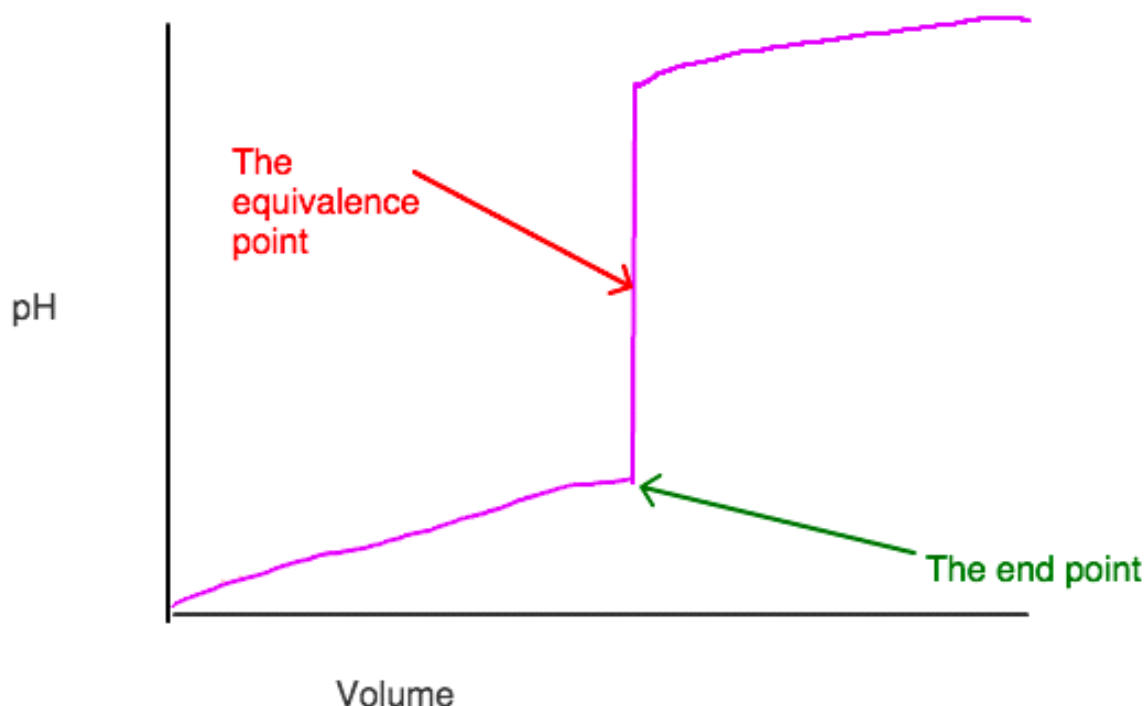
a naturally occurring solid material from which a metal or valuable mineral can be profitably extracted.

 Translations, word origin, and more definitions

Question 5 (e)

- (e) What is the difference between the equivalence point of a titration and the end point of a titration?

<p>The equivalence point in a titration occurs when the number of moles of titrant added is exactly sufficient to react completely with the number of moles of the titrated species present in the sample being titrated.</p> <p>The end point of a titration is the point in a titration at which the indicator undergoes its color change.</p>	<p>One point is earned for each correct definition.</p>
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Question 6 (g)

(g) Is the oxygen atom, O, a catalyst for the reaction or is it an intermediate? Explain.

The O atom is an intermediate because it is formed and then consumed during the course of the reaction. (Had it been a catalyst, it would have been present both at the beginning and the end of the reaction.)

One point is earned for the correct choice with explanation.

both catalysts and intermediates cancel in net reaction

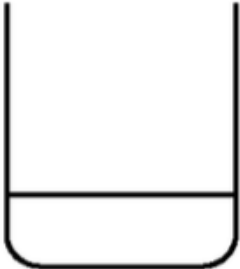
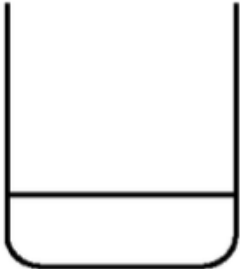
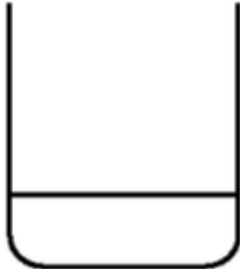
intermediate (ClO): generated in an earlier step, consumed in a later step

catalyst (Cl): consumed in an earlier step, released (regenerated) in a later step

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Question 1 (c)

<p>Beaker 1</p> 	<p>Beaker 2</p> 	<p>Beaker 3</p> 
<p>0.100 M HCl</p>	<p>0.100 M NH₃</p>	<p>0.100 M NH₄Cl</p>

- (ii) The contents of beaker 2 are poured into beaker 3 and the resulting solution is stirred. Assume that volumes are additive. Calculate the pH of the resulting solution.

In the resulting solution, $[\text{NH}_3] = [\text{NH}_4^+]$;

$$K_a = 5.6 \times 10^{-10} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

Thus $[\text{H}_3\text{O}^+] = 5.6 \times 10^{-10}$; $\text{pH} = -\log(5.6 \times 10^{-10}) = 9.25$

1 point is earned for noting that the solution is a buffer with $[\text{NH}_3] = [\text{NH}_4^+]$.

1 point is earned for the correct pH.

- Henderson–Hasselbalch equation



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

$$\log_{10} K_a = \log_{10} [\text{H}^+] + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$$

$$-\text{p}K_a = -\text{pH} + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]}$$

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{A}^-]}{[\text{HA}]} \quad (1)$$

Question 1 (d)

(ii) Calculate the final $[\text{NH}_4^+]$ in the resulting solution at 25°C.

<p>moles = (volume)(molarity)</p> <p>moles H_3O^+ in sol. 1 = $(0.0250)(0.100) = 0.00250 \text{ mol}$</p> <p>moles NH_3 in sol. 2 = $(0.0250)(0.100) = 0.00250 \text{ mol}$</p> <p>moles NH_4^+ in sol. 3 = $(0.0250)(0.100) = 0.00250 \text{ mol}$</p> <p><u>When the solutions are mixed, the H_3O^+ and NH_3 react to form NH_4^+, resulting in a total of 0.00500 mol NH_4^+. The final volume is the sum $(25.0 + 25.0 + 25.0) = 75.0 \text{ mL}$.</u></p> <p>The final concentration of $\text{NH}_4^+ = (0.00500 \text{ mol}/0.0750 \text{ L}) = 0.0667 \text{ M}$.</p>	<p>1 point is earned for the correct calculation of moles of NH_4^+.</p> <p>1 point is earned for the correct calculation of the final volume <u>and</u> concentration.</p>
---	---

Question 2 (a)

- Your answers should have the same decimal places as the equipment can read

- (i) Calculate the volume, in mL, of 16 M HNO₃ that the student should use for preparing 50. mL of 6 M HNO₃.

moles before dilution = moles after dilution $M_i V_i = M_f V_f$ $(16\text{ M})(V_i) = (6\text{ M})(50.\text{ mL})$ $V_i = 19\text{ mL or }20\text{ mL (to one significant figure)}$	1 point is earned for the correct volume.
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- Procedure for preparing solutions

- (ii) Briefly list the steps of an appropriate and safe procedure for preparing the 50. mL of 6 M HNO₃. Only materials selected from those provided to the student (listed above) may be used.

Wear <u>safety goggles and rubber gloves</u> . Then measure 19 mL of 16 M HNO ₃ using a 100 mL graduated cylinder. Measure 31 mL of distilled H ₂ O using a 100 mL graduated cylinder. Transfer the water to a 100 mL beaker. Add the acid to the water <u>with stirring</u> .	1 point is earned for properly measuring the volume of 16 M HNO ₃ and preparing a 6 M HNO ₃ acid solution. 1 point is earned for wearing protective gear and for adding acid to water.
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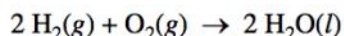
- Volumetric flask vs. Graduated cylinder

- (iii) Explain why it is not necessary to use a volumetric flask (calibrated to 50.00 mL ±0.05 mL) to perform the dilution.

The graduated cylinders provide <u>sufficient precision</u> in volume measurement to provide two significant figures, making the use of the volumetric flask unnecessary.	1 point is earned for an acceptable explanation.
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Question 3 (a)

- Notice the **coefficient** of the reactants and products in calculating standard enthalpy change
- Standard enthalpy of formation of **pure elements** in their standard states are assigned **zero**



- (a) Calculate the standard enthalpy change, ΔH_{298}° , for the reaction represented by the equation above.

(The molar enthalpy of formation, ΔH_f° , for H₂O(l) is -285.8 kJ mol⁻¹ at 298 K.)

$\Delta H_{298}^\circ = [2(-285.8)] - [2(0) + 1(0)] = -571.6\text{ kJ mol}^{-1}$	1 point is earned for the correct answer.
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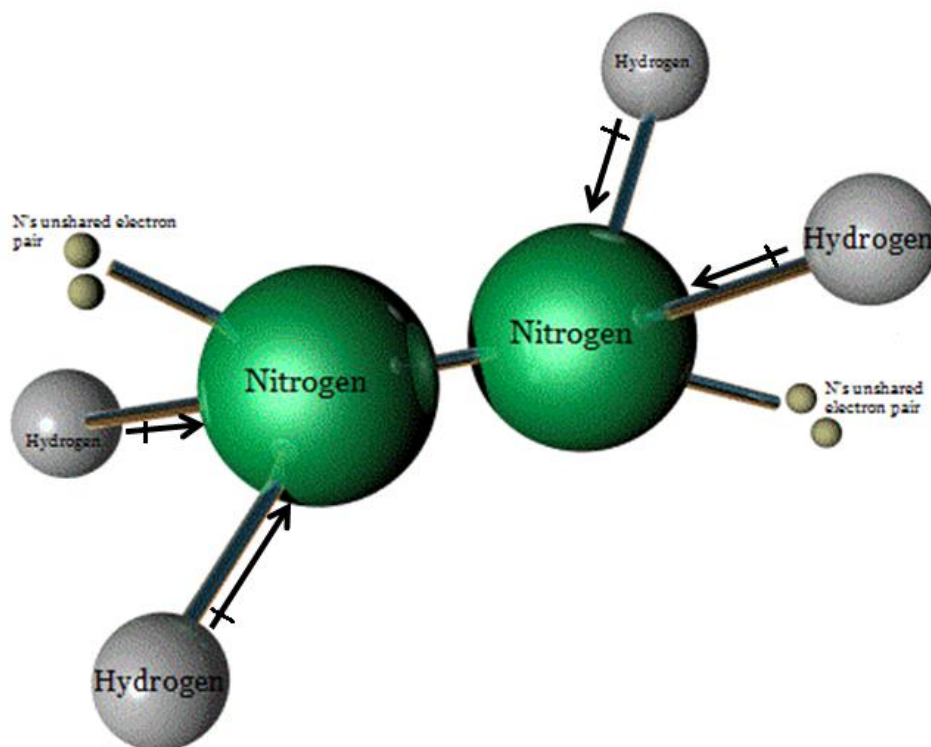
Question 5 (b)

(b) On the basis of the diagram you completed in part (a), do all six atoms in the N_2H_4 molecule lie in the same plane? Explain.

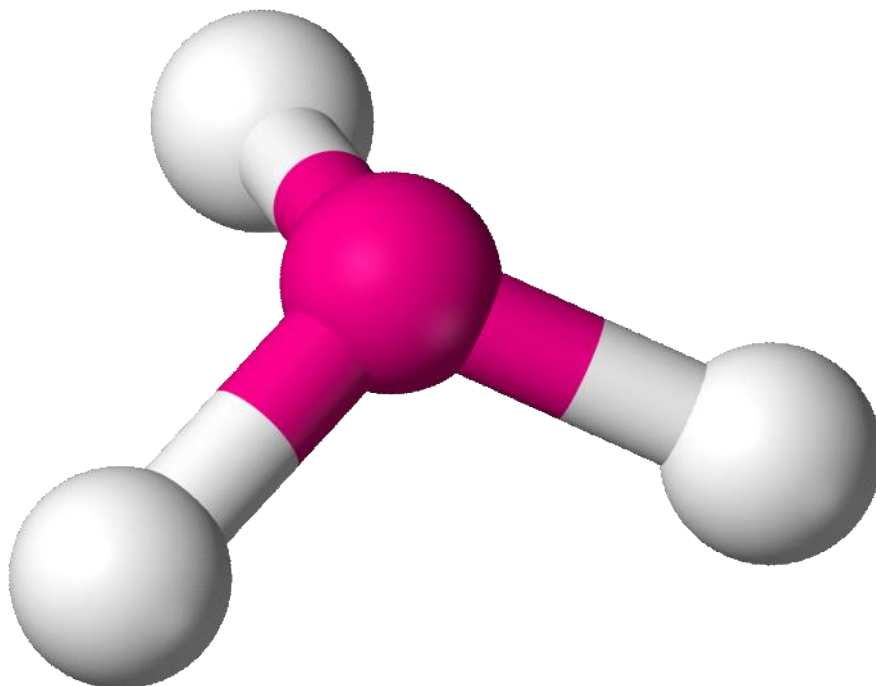
No, they do not. The molecular geometry surrounding both nitrogen atoms is trigonal pyramidal. Therefore the molecule as a whole cannot have all the atoms in the same plane.

1 point is earned for a correct answer with a valid explanation.

- N_2H_4 molecular geometry



- Trigonal pyramidal



Question 5 (c)






- (c) The normal boiling point of N_2H_4 is 114°C , whereas the normal boiling point of C_2H_6 is -89°C . Explain, in terms of the intermolecular forces present in each liquid, why the boiling point of N_2H_4 is so much higher than that of C_2H_6 .

N_2H_4 is a polar molecule with London dispersion forces, dipole-dipole forces, and hydrogen bonding between molecules, whereas C_2H_6 is nonpolar and only has London dispersion forces between molecules. It takes more energy to overcome the stronger IMFs in hydrazine, resulting in a higher boiling point.

1 point is earned for correct reference to the two different types of IMFs.

1 point is earned for a valid explanation based on the relative strengths of the IMFs.

Nonbonding (Intermolecular)

Ion-dipole		Ion charge– dipole charge	40–600	$\text{Na}^+ \cdots \text{O} \begin{array}{l} \text{H} \\ \text{H} \end{array}$
H bond	$\delta^- \quad \delta^+ \quad \delta^-$ $-\text{A}-\text{H} \cdots \cdots \text{:B}-$	Polar bond to H– dipole charge (high EN of N, O, F)	10–40	$\begin{array}{c} \text{:}\ddot{\text{O}}-\text{H} \cdots \cdots \text{:}\ddot{\text{O}}-\text{H} \\ \qquad \qquad \\ \text{H} \qquad \qquad \text{H} \end{array}$
Dipole-dipole		Dipole charges	5–25	$\text{I}-\text{Cl} \cdots \cdots \text{I}-\text{Cl}$
Ion–induced dipole		Ion charge– polarizable e^- cloud	3–15	$\text{Fe}^{2+} \cdots \cdots \text{O}_2$
Dipole–induced dipole		Dipole charge– polarizable e^- cloud	2–10	$\text{H}-\text{Cl} \cdots \cdots \text{Cl}-\text{Cl}$
Dispersion (London)		Polarizable e^- clouds	0.05–40	$\text{F}-\text{F} \cdots \cdots \text{F}-\text{F}$

Question 6 (b)

(b) The flask is then heated to 45°C, and the pressure in the flask increases. In terms of kinetic molecular theory, provide TWO reasons that the pressure in the flask is greater at 45°C than at 35°C.

There are three possible reasons based on kinetic molecular theory.

- At the higher temperature there are more ethanol molecules in the gas phase, so there will be more collisions with the flask walls, resulting in a greater pressure.
- At the higher temperature the molecules will be moving faster on average, thus colliding with the flask walls more frequently, resulting in a greater pressure.
- Because the molecules are moving faster on average, their collisions with the flask walls will exert a greater force, resulting in a greater pressure.

1 point is earned for each correct reason up to a maximum of 2 points.

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Question 2 (c)

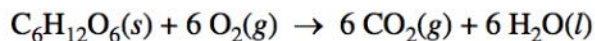
- (c) The tank is cooled to 25°C, which is well below the boiling point of methanol. It is found that small amounts of H₂(g) and CO(g) have dissolved in the liquid CH₃OH. Which of the two gases would you expect to be more soluble in methanol at 25°C? Justify your answer.

The only attractive forces between molecules of H₂ and CH₃OH would be due to weak London dispersion forces (LDFs). In contrast, the LDFs are stronger between CO molecules and CH₃OH molecules because CO has more electrons than H₂. In addition CO is slightly polar; thus intermolecular dipole-dipole attractions can form between CO molecules and CH₃OH molecules. With stronger intermolecular interactions between molecules of CO and CH₃OH, CO would be expected to be more soluble in CH₃OH than H₂.

1 point is earned for the correct answer and justification.

Question 3 (b)

In many organisms, glucose is oxidized to carbon dioxide and water, as represented by the following equation.



A 2.50 g sample of glucose and an excess of O₂(g) were placed in a calorimeter. After the reaction was initiated and proceeded to completion, the total heat released by the reaction was calculated to be 39.0 kJ.

- (b) Calculate the value of ΔH° , in kJ mol⁻¹, for the combustion of glucose.

$$2.50 \text{ g} \times \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.16 \text{ g C}_6\text{H}_{12}\text{O}_6} = 0.0139 \text{ mol C}_6\text{H}_{12}\text{O}_6$$

$$\frac{-39.0 \text{ kJ}}{0.0139 \text{ mol}} = -2,810 \text{ kJ mol}^{-1}$$

1 point is earned for the correct answer.

Question 5 (b)

- (b) Describe the steps in a procedure to prepare 100.0 mL of 1.250 *M* NaOH solution using 5.000 *M* NaOH and equipment selected from the list below.

Balance	25 mL Erlenmeyer flask	100 mL graduated cylinder	100 mL volumetric flask
50 mL buret	100 mL Florence flask	25 mL pipet	100 mL beaker
Eyedropper	Drying oven	Wash bottle of distilled H ₂ O	Crucible

Pipet 25.00 mL of 5.000 *M* NaOH solution into the 100 mL volumetric flask.

Fill the volumetric flask to the calibration line with distilled water; using an eyedropper for the last few drops is advised.

Cap the volumetric flask and invert several times to ensure homogeneity.

1 point is earned for descriptions of any two of the three steps.

An additional point is earned if all three steps are described.

- Eyedropper



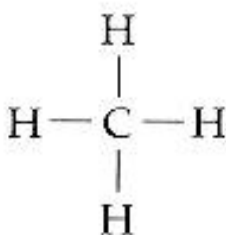
Question 6 (a)

- (ii) Estimate the numerical value of the $\text{H}_y\text{-C}_x\text{-O}$ bond angle in an ethyl methanoate molecule.
Explain the basis of your estimate.

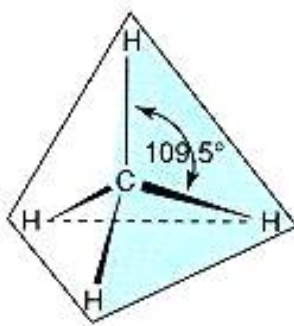
The C_x is the central atom in a tetrahedral arrangement of bonding electron pairs; thus the angle would be approximately 109.5° .

1 point is earned for the correct angle with an appropriate explanation.

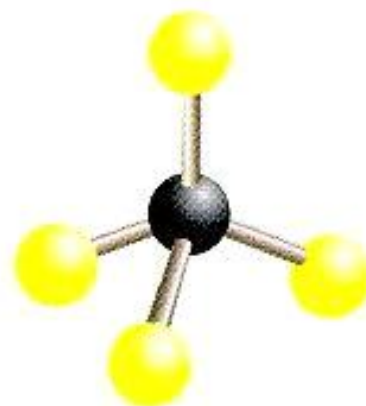
structural
formula



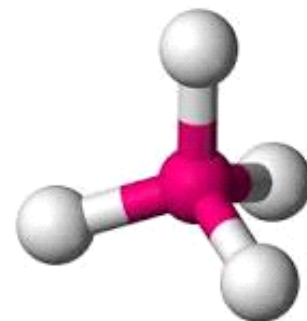
molecular
shape



ball-and-stick
model



In a tetrahedral molecular geometry, a central atom is located at the center with four substituents that are located at the corners of a tetrahedron. The bond angles are $\cos^{-1}(-1/3) = 109.4712206...^\circ \approx 109.5^\circ$ when all four substituents are the same, as in methane (CH_4) as well as its heavier analogues.



Tetrahedral molecular geometry - Wikipedia

https://en.wikipedia.org/wiki/Tetrahedral_molecular_geometry

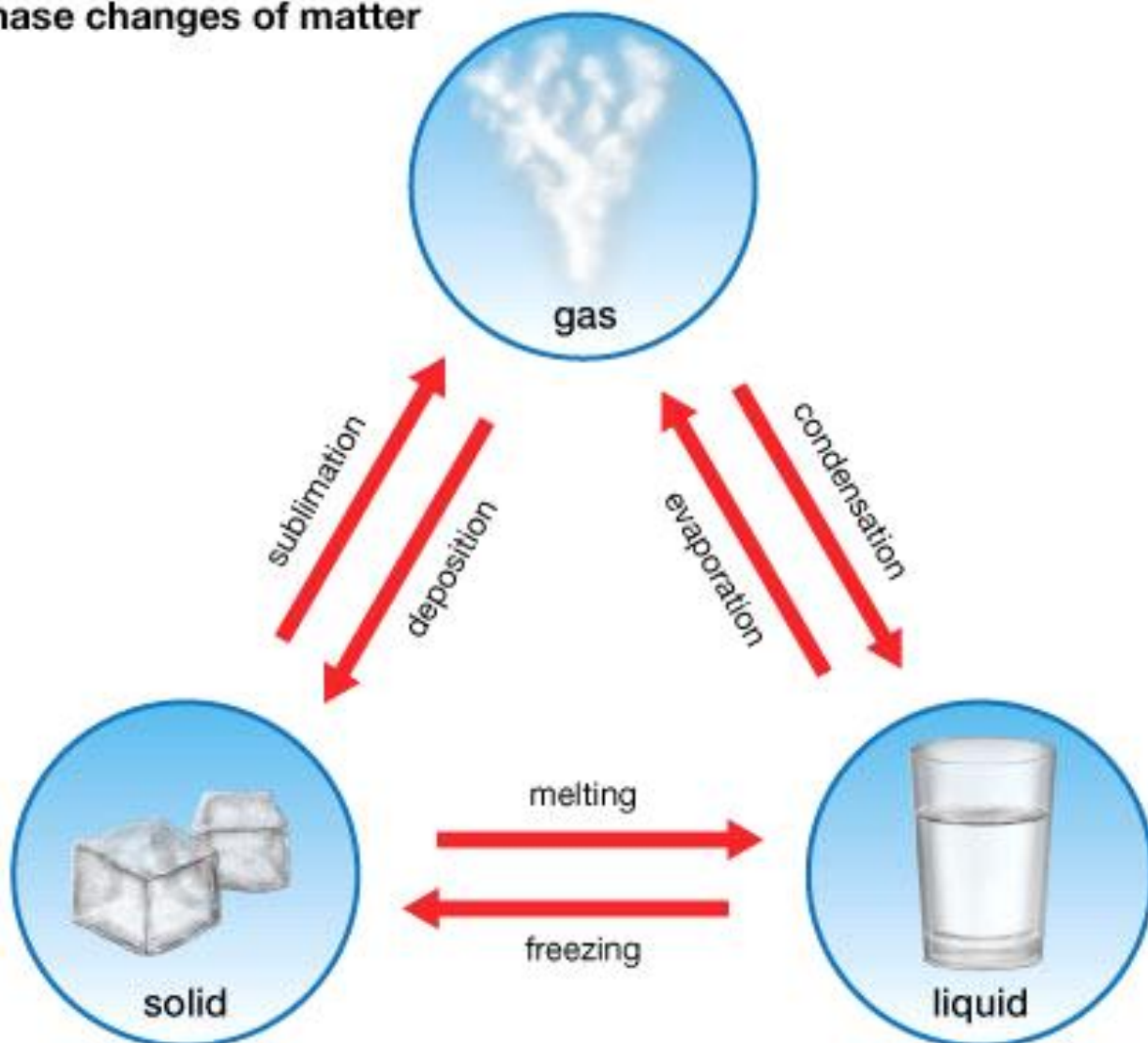
Question 6 (c)

- (ii) Explain, in terms of processes occurring at the molecular level, why the pressure in the flask remained constant after 60. seconds.

At the equilibrium vapor pressure, the rate of molecules passing from the liquid to the gas phase (vaporizing) equals the rate of gas phase molecules passing into the liquid phase (condensing).

1 point is earned for the correct explanation.

Phase changes of matter



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- (iv) After 80. seconds, additional liquid ethyl methanoate is added to the container at 20°C. Does the partial pressure of the ethyl methanoate vapor in the container increase, decrease, or stay the same? Explain. (Assume that the volume of the additional liquid ethyl methanoate in the container is negligible compared to the total volume of the container.)

The partial pressure of the vapor stays the same because the equilibrium vapor pressure for 20°C has already been reached. Because the temperature remains constant, the vapor pressure would remain unchanged.

1 point is earned for the correct answer with an explanation.


2012 Multiple Choice

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Question 3

- There is no molecular in ionic compound, neither does INTRAMOLECULAR force.

Question 8

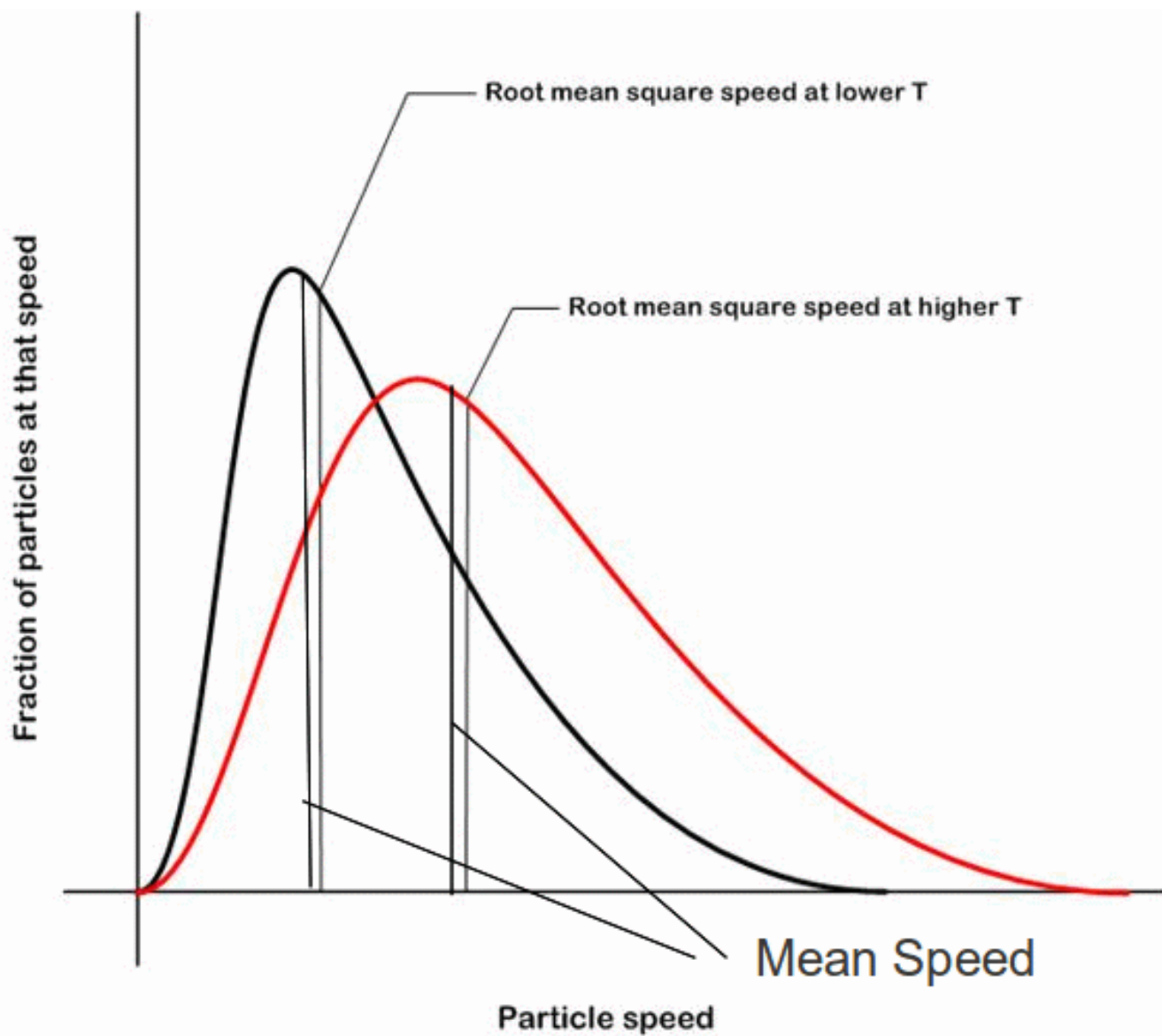
- Hydrolysis and Brønsted–Lowry acid–base reaction
- 

Hydrolysis of Ions

- There are many ionic salt's that make the aqueous solution acidic or basic.
- The reaction of ionic salts with water is called "Hydrolysis of salts"
- Hydrolysis can be explained using Brønsted Lowry theory.
- If the conjugate acid or base is strong then there will be hydrolysis.
- Weak acids and bases produce strong conjugate bases and acids

Question 10

- Root-mean-square speed



Uses of RMS Velocity

- RMS speed is used to predict how fast molecules are moving at a given Temperature.

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$

$$v_{rms} = \sqrt{\frac{3RT}{M}}$$

How fast molecules move is directly proportional to their absolute temperature and inversely proportional to their mass.

Because: $k = \frac{R}{N_A}$ then $\frac{k}{m} = \frac{R}{M}$

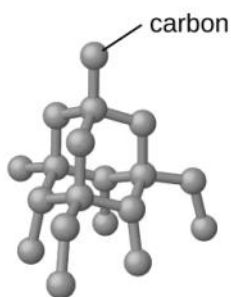
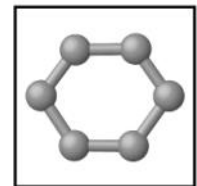
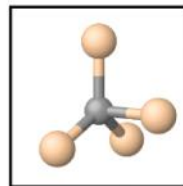
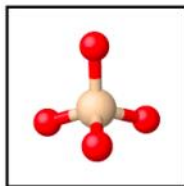
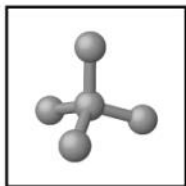
Question 17

STRUCTURE & PROPERTIES OF SOLIDS

Summary:

Ionic	Metals	Molecular	Covalent Network
<ul style="list-style-type: none"> Electrically conductive if molten Brittle Usually crystalline High melting point (solids at SATP) 	<ul style="list-style-type: none"> Electrically and heat conductive Malleable and ductile Lustrous and hard Medium to high melting points (solid at SATP) 	<ul style="list-style-type: none"> Non-conductive Amorphous Non crystalline usually Low melting point (liquid or gas) 	<ul style="list-style-type: none"> Sometimes conductive (C) Rigid to flexible Patterned spatial bonds Medium to high melting points

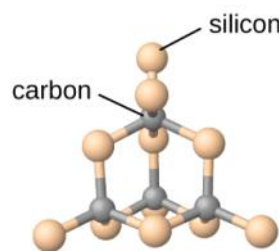
• Covalent network solid



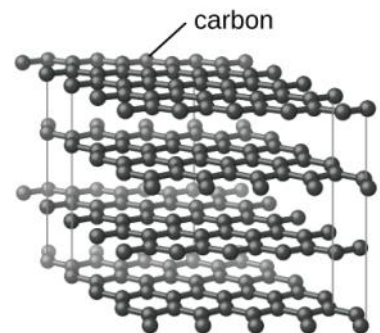
diamond



silicon dioxide



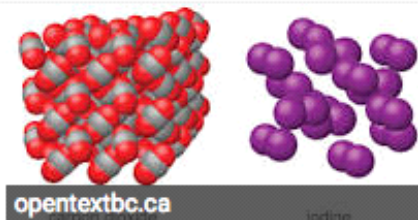
silicon carbide



graphite

• Molecular solid

Molecular solids are **solids** that are essentially collections of molecules held together by intermolecular forces (IMFs). The **solid** structure is maintained by IMFs rather than bonds (metallic, covalent, or ionic). The forces holding the **solids** together are much weaker than for other types of **solids**.



Molecular solids - Chemistry 301

<https://ch301.cm.utexas.edu/section2.php?target=imfs/solids/molecular-solids.html>

Question 48

When a buret is rinsed before a titration, which of the techniques below is the best procedure?

- (A) Rinse the buret one time with some of the titrant solution.
- (B) Rinse the buret one time with some of the titrant solution and then dry the buret in an oven.
- (C) Rinse the buret two times: once with some of the titrant solution, then once with distilled water.
- (D) Rinse the buret two times: each time with some of the titrant solution.
- (E) Rinse the buret two times: each time with distilled water.

2012 Free Response

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Question 1 (e)

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

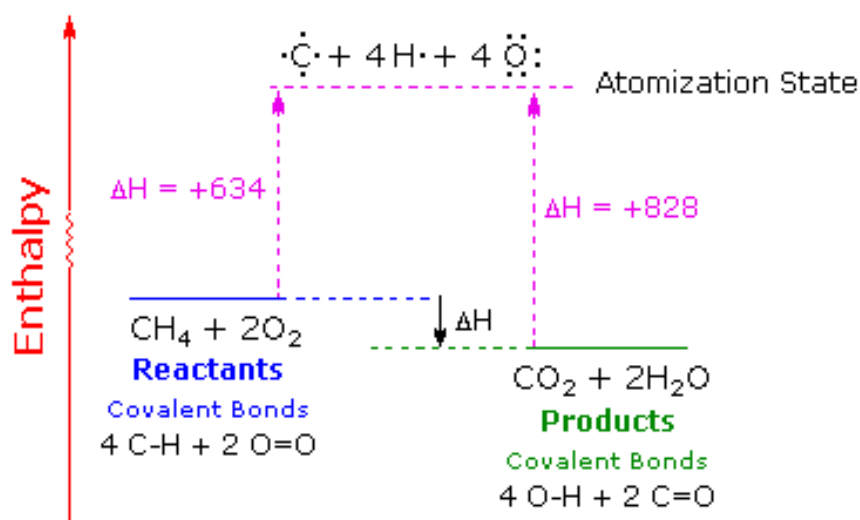
$$6.3 \times 10^{-5} = \frac{(x)(x)}{(0.200 - x)}; \text{ assume that } x \ll 0.200 \text{ M}$$

$$x = [\text{H}_3\text{O}^+] = 3.5 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(3.5 \times 10^{-3}) = 2.45$$

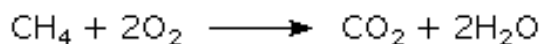
Question 3 (b)

- ΔH° = enthalpy of bonds broken - enthalpy of bonds formed



Average Bond Energies

O=O	119 kcal/mol
C-H	99
O-H	111
C=O (in CO_2)	192



$$-[\Sigma(\text{Product Bond Energies}) - \Sigma(\text{Reactant Bond Energies})] = \Delta H_{\text{(reaction)}}$$

$$-[(444 + 384) - (396 + 238)] = -[828 - 634] = -194 \text{ kcal/mol}$$

Correcting for the heat of condensation of 2 H_2O product molecules $2(-10.5)$

$$\Delta H^\circ = -194 - 21 = -215 \text{ kcal/mol}$$

Question 3 (d)

Reaction	Order	Units of rate constant
Zero order reaction	0	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^0} = \text{mol L}^{-1} \text{s}^{-1}$
First order reaction	1	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^1} = \text{s}^{-1}$
Second order reaction	2	$\frac{\text{mol L}^{-1}}{\text{s}} \times \frac{1}{(\text{mol L}^{-1})^2} = \text{mol}^{-1} \text{L s}^{-1}$

Question 5 (c)

- (c) $\text{I}_2(\text{s})$ and $\text{Br}_2(\text{l})$ can react to form the compound $\text{IBr}(\text{l})$. Predict which would have the greater molar enthalpy of vaporization, $\text{IBr}(\text{l})$ or $\text{Br}_2(\text{l})$. Justify your prediction.

$\text{IBr}(\text{l})$. Two reasons may be given. First, IBr is polar, and dipole-dipole forces would tend to increase the enthalpy of vaporization. Second, IBr should have stronger London dispersion forces because of the greater number of electrons in the larger IBr molecule.

1 point is earned for the correct choice with either or both of the acceptable reasons.

Question 5 (d)

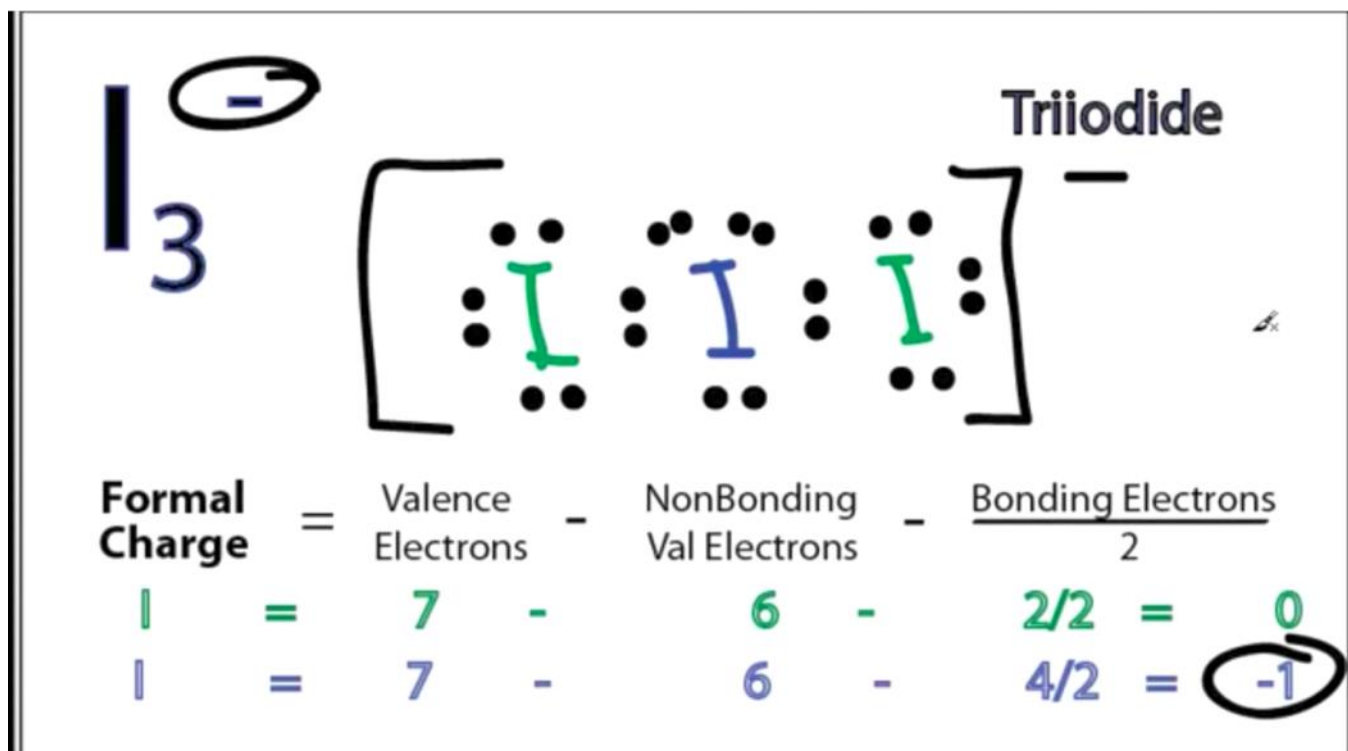
- (d) Explain why the hexane layer is light purple while the water layer is virtually colorless. Your explanation should reference the relative strengths of interactions between molecules of I_2 and the solvents H_2O and C_6H_{14} , and the reasons for the differences.

The hexane layer is purple because most of the I_2 is dissolved in it. The entrance of the I_2 into water requires disruption of the hydrogen bonds in water, which are much stronger than the London dispersion forces in hexane. Meanwhile, the London dispersion forces between I_2 and hexane would be stronger than the London dispersion forces between I_2 and water. (Water and I_2 can also interact through a dipole-induced dipole force, but this attraction is insufficient to overcome the other differences noted above.)

1 point is earned for recognizing from the experimental observations that the iodine dissolved in the hexane.

1 point is earned for a correct explanation referencing the differences between water and hexane in their interactions with I_2 .

Question 5 (e)



(ii) In which layer, water or hexane, would the concentration of I_3^- be higher? Explain.

I_3^- would be more soluble in water because of the ion-dipole interactions that would occur between the ions and the polar water molecules. No such interactions are possible in the nonpolar hexane.

1 point is earned for the correct choice and explanation.

Question 6 (c)

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

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

Question 6 (e)

- (i) A student bumps the cell setup, resulting in the salt bridge losing contact with the solution in the cathode compartment. Is V equal to 0.47 or is V equal to 0? Justify your choice.

$V = 0$ V. The transfer of ions through the salt bridge will stop. A charge imbalance between the half-cells will prevent electrons from flowing through the wire.

1 point is earned for the correct choice with an appropriate explanation.

- (ii) A student spills a small amount of $0.5\text{ M Na}_2\text{SO}_4(aq)$ into the compartment with the Pb electrode, resulting in the formation of a precipitate. Is V less than 0.47 or is V greater than 0.47? Justify your choice.

$V > 0.47$ V. The sulfate ion will react with the Pb^{2+} ion to form a precipitate. This results in a thermodynamically favored anode half-cell reaction and hence a larger potential difference. The choice may also be justified using the Nernst equation.

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \left(\frac{RT}{nF} \right) \ln \frac{[\text{Pb}^{2+}]}{[\text{Cu}^{2+}]}$$

Decreasing the $[\text{Pb}^{2+}]$ will increase the cell voltage.

1 point is earned for the correct choice with an appropriate explanation.

- (iii) After the laboratory session is over, a student leaves the switch closed. The next day, the student opens the switch and reads the voltmeter. Is V less than 0.47 or is V equal to 0.47? Justify your choice.

$V < 0.47$ V. Over time, $[\text{Pb}^{2+}]$ increases and $[\text{Cu}^{2+}]$ decreases, making both half-cell reactions less thermodynamically favorable. The choice may also be justified using the Nernst equation. Increasing $[\text{Pb}^{2+}]$ and decreasing $[\text{Cu}^{2+}]$ decreases the cell voltage. The choice may also be justified by stating that the voltage is zero as a result of the establishment of equilibrium.

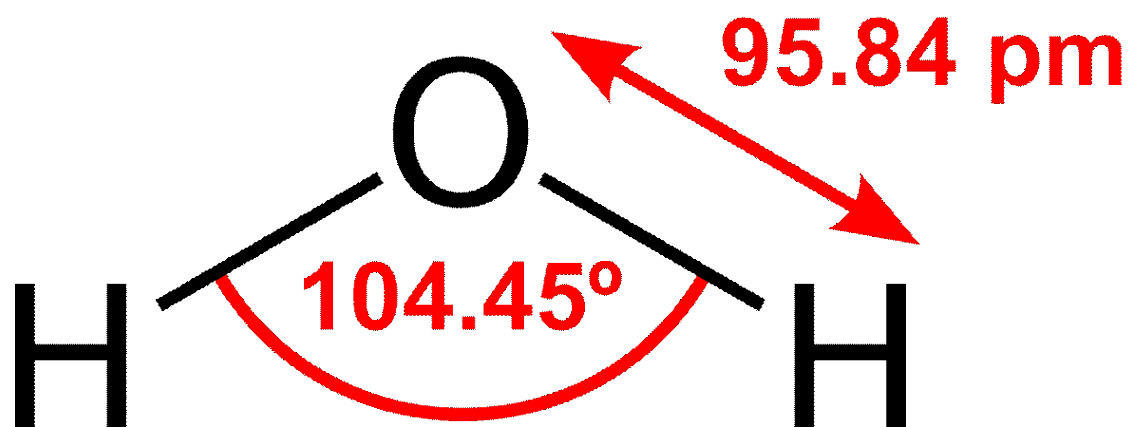
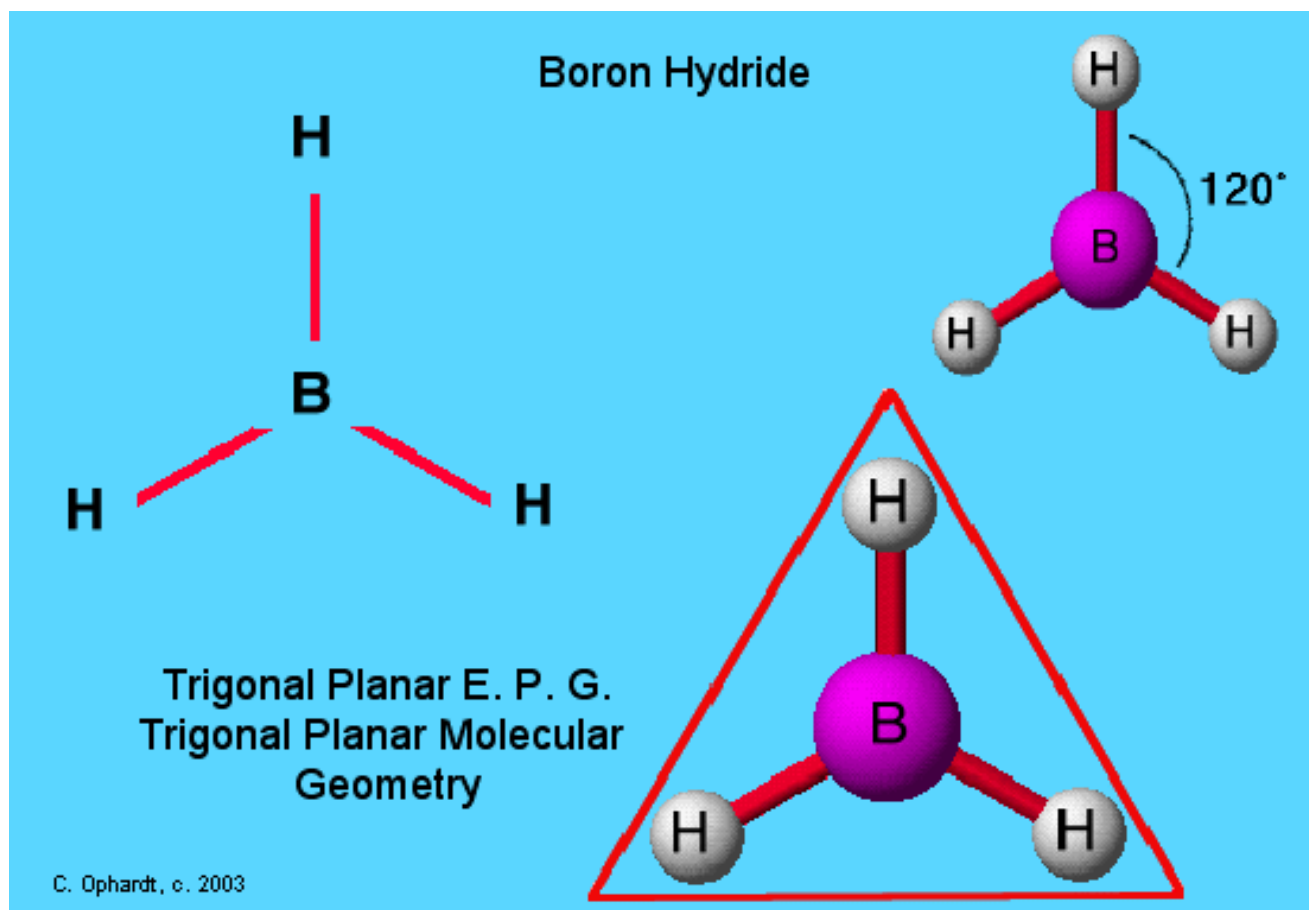
1 point is earned for the correct choice with an appropriate explanation.

2013 Multiple Choice

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Question 6

- Bond angle



Question 33

- Erlenmeyer flask

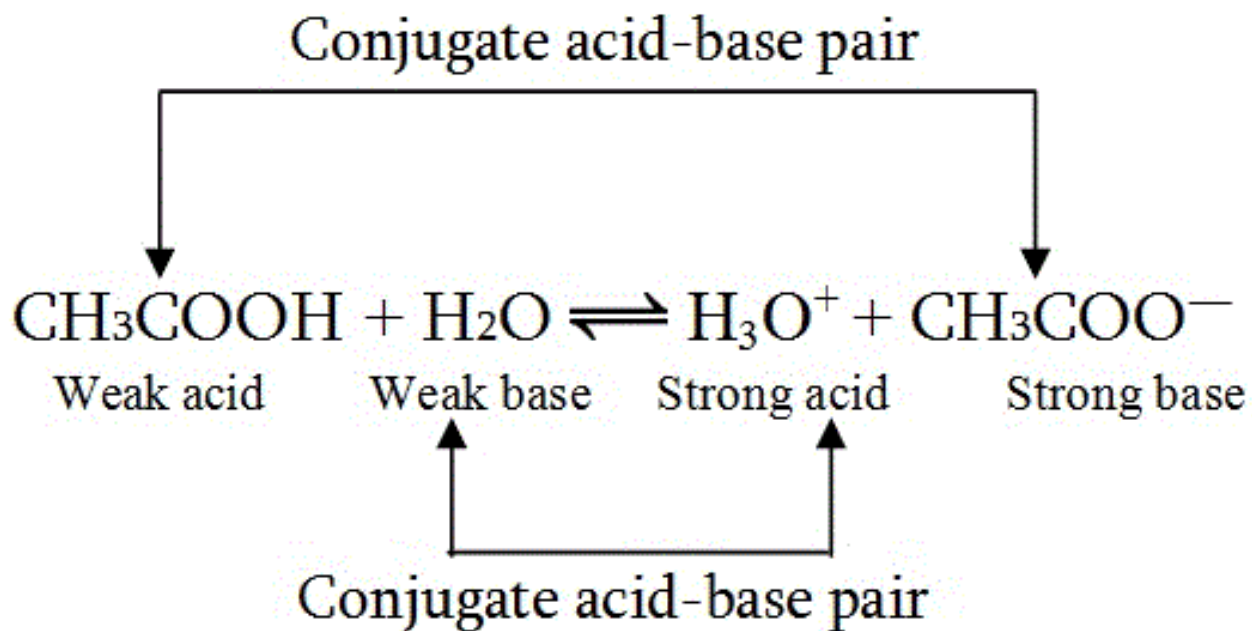


- Volumetric flask



Question 40

- Strong + Strong --> Weak + Weak



Question 42

- The order of Boiling point: HF > HI > HBr > HCl

Now, it must intuitively be certain that more the number of electrons then more the amount of **London dispersion forces**. This is true; the more the electrons the atom has, the stronger the amount of London dispersion forces and hence greater the attraction. The greater the attraction, the more energy you have to put to break the bonds apart. If you see the trend above, Iodine has more electrons than Bromine hence has a greater attraction force between its atoms hence has a greater boiling point. Similar for the case of Bromine and Chlorine. Hence, you can place the order of their boiling points as:



Hence,

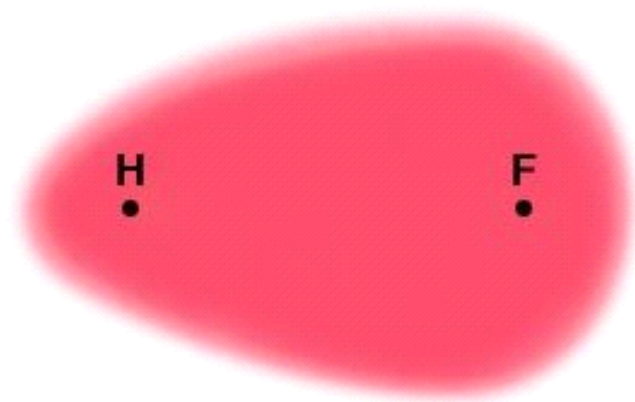


However, you notice an anomaly; HF should have a boiling point below that of HCl, then how come it has the highest boiling point? After all, Fluorine has lesser electrons than Chlorine and hence should have lesser London dispersion forces between them. This is true but there is another reason behind that: **Hydrogen Bonding**.

Picture fluorine; it sits right above the other halogens. It belongs to Period 2 which does not have many shells to itself. Since it has so less electrons, it must be very small. In fact, it is. Fluorine is so small yet it has a really high charge density. Why does it have a high charge density? Its outer electrons are not as shielded by the inner electrons and it has 7 outer electrons. (read more on: [Shielding effect](#) ↗) These seven electrons face tremendous attraction from its nucleus hence it 'shrinks'. This causes the fluorine atom to shrink hence its charge density increases. As such, it can attract other electrons to itself when it is covalently bonded to another element. This property is called **electronegativity**.

Now, this effect is very strong in case of smaller atoms like Fluorine. When fluorine is bonded with Hydrogen, it attracts certain portion of the bonded electrons to itself. This effect is strong enough that it stays like that permanently but since the electrons are always moving, it must mean that the electrons love to spend more 'time' with fluorine than hydrogen. When this happens, a permanent dipole is created since the electrons are not evenly distributed. As such, two charges are created in the two ends: $\delta+$ and $\delta-$

Electron Density Distribution

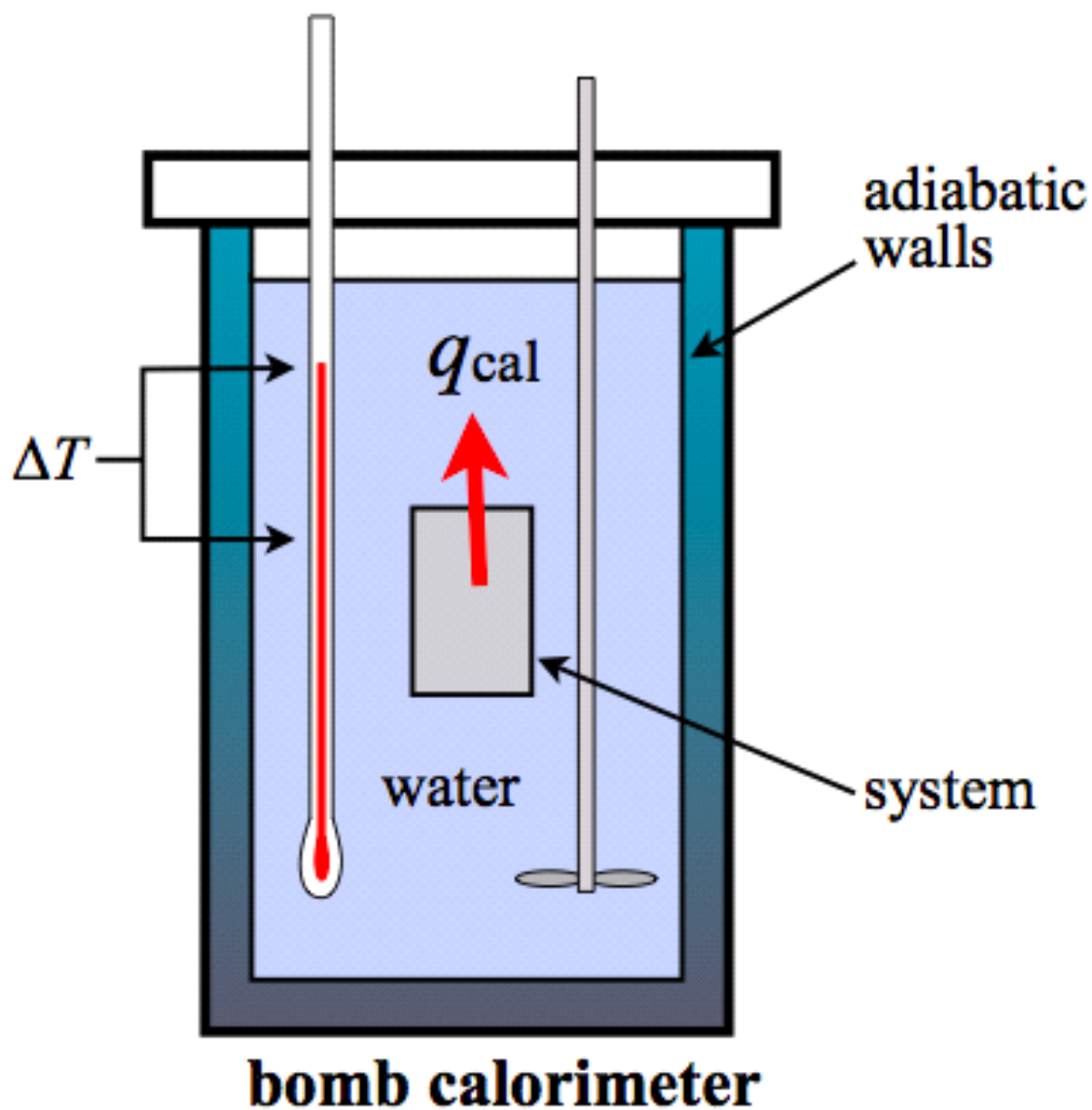


As you know, charges attract each other. Since the fluorine atom is so electronegative, this charge difference must be very great. Since the difference is so great, this attraction effect is very strong. As such, these molecules of HF start to 'clump' together (since they attract each other) in what is known as **hydrogen bonding**. Hydrogen bonding is the attraction between highly electronegative atoms with hydrogen bonded covalently.

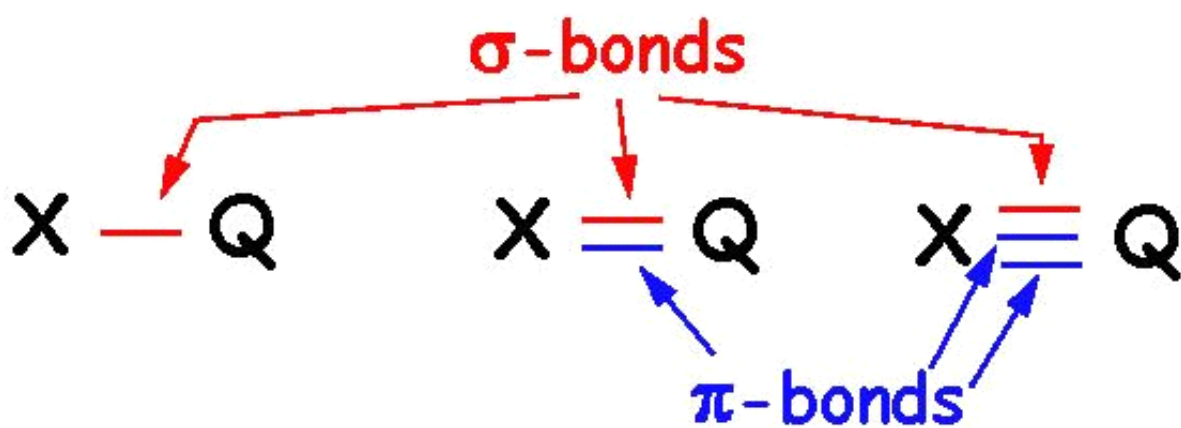
This attraction is stronger than London dispersion forces hence the presence of a hydrogen bond significantly raises the boiling point of the compound. Hence, HF has the highest boiling point amongst the four compounds.

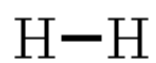
Question 65

- Calorimetry

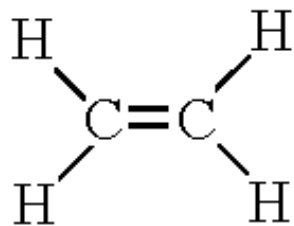


Question 71





1 σ bond



1 σ bond

1 π bond



1 σ bond

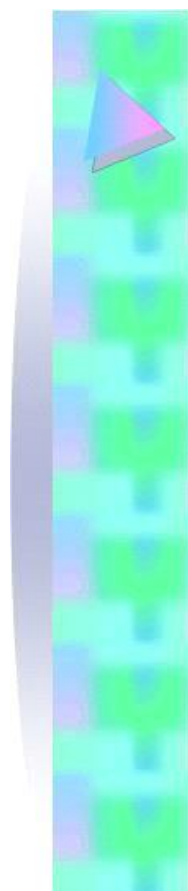
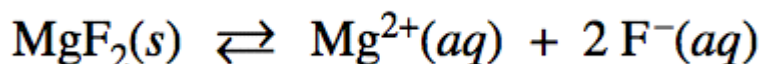
2 π bonds

2013 Free Response

Tuesday, April 4, 2017 9:42 PM

Question 1 (a)

- Write the state of each substance for dissolving equation



The Solubility Expression



$$K_{sp} = [\text{A}^{b+}]^a [\text{B}^{a-}]^b$$



$$K_{sp} = [\text{Pb}^{2+}] [\text{I}^{-}]^2$$

❖ The greater the k_{sp} the more soluble the solid is in H_2O .

Question 1 (b)

- (ii) Calculate the minimum concentration of $\text{F}^{-}(aq)$ necessary to initiate precipitation of the salt selected in part (b)(i).

$$K_{sp} = 3.5 \times 10^{-11} = [\text{Ca}^{2+}][\text{F}^{-}]^2 = (0.10)[\text{F}^{-}]^2$$

$$3.5 \times 10^{-10} = [\text{F}^{-}]^2$$

$$[\text{F}^{-}] = \sqrt{3.5 \times 10^{-10}} = 1.9 \times 10^{-5} M$$

1 point is earned for the correct value of $[\text{F}^{-}]$.

Question 3 (c)

- (c) Calculate the magnitude of q , the thermal energy change, when the MgO was added to the 1.0 M HCl(aq) . Include units with your answer.

$q_{\text{calorimeter}} = q_{\text{cal}} = mc\Delta T$ In trial 2, $q_{\text{cal}} = \left[\left(100.0\text{ mL} \times \frac{1.0\text{ g}}{\text{mL}} \right) + 0.50\text{ g} \right] \left(\frac{4.18\text{ J}}{\text{g} \cdot ^\circ\text{C}} \right) (4.1^\circ\text{C}) = 1700\text{ J or }1.7\text{ kJ}$ OR In trial 3, $q_{\text{cal}} = \left[\left(100.0\text{ mL} \times \frac{1.0\text{ g}}{\text{mL}} \right) + 0.25\text{ g} \right] \left(\frac{4.18\text{ J}}{\text{g} \cdot ^\circ\text{C}} \right) (2.1^\circ\text{C}) = 880\text{ J or }0.88\text{ kJ}$ OR In trial 4, $q_{\text{cal}} = \left[\left(100.0\text{ mL} \times \frac{1.0\text{ g}}{\text{mL}} \right) + 0.50\text{ g} \right] \left(\frac{4.18\text{ J}}{\text{g} \cdot ^\circ\text{C}} \right) (4.0^\circ\text{C}) = 1700\text{ J or }1.7\text{ kJ}$	<div style="border: 1px solid red; padding: 5px; margin-bottom: 10px;"> 1 point is earned for the correct mass of the solution. </div> 1 point is earned for the correct calculation of q for any trial with a valid ΔT and correct units.
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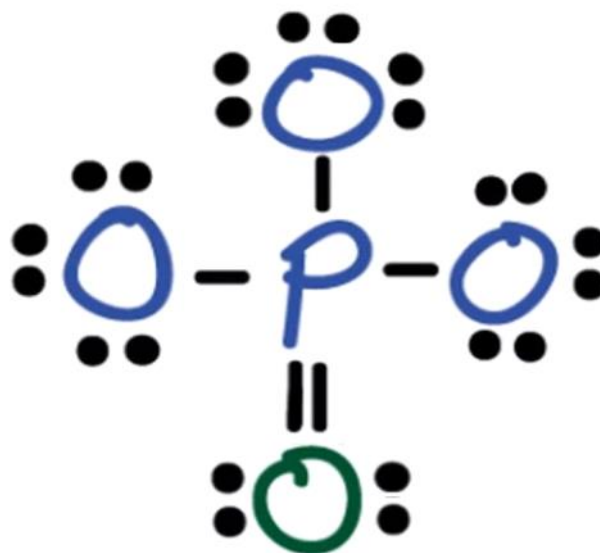
Question 3 (e)

$$q_{\text{rxn}} = -q_{\text{cal}}$$

Question 4 (a)



Phosphate Ion



- Write ionic equation if possible

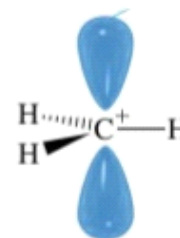
Question 5 (a)

- (a) Describe TWO reasons why the pressure changes as the temperature of the $C_2H_4(g)$ increases. Your descriptions must be in terms of what occurs at the molecular level.

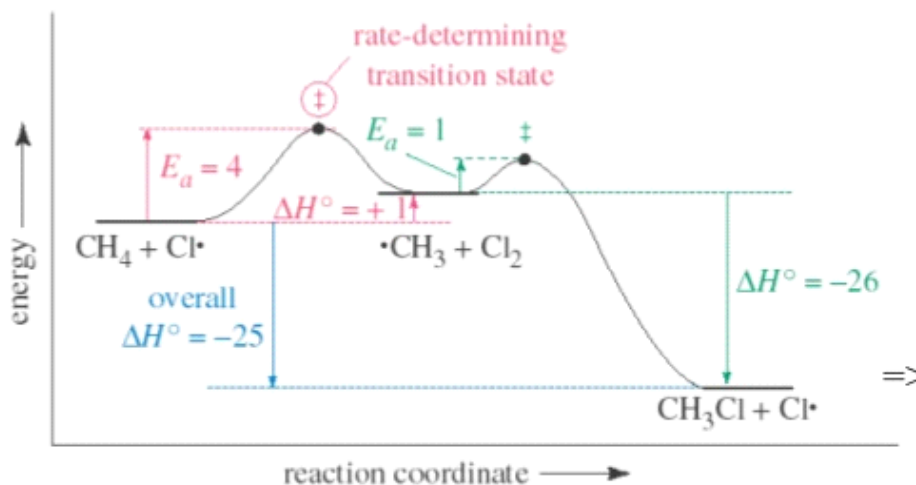
Two reasons are:	
(1) As the temperature increases, the <u>average speed</u> of the molecules increases and the molecules collide <u>more frequently</u> with the container walls.	1 point is earned for <u>each</u> correct reason.
(2) As the temperature increases, the <u>average kinetic energy</u> of the molecules increases and the molecules strike the walls of the container with <u>greater force</u> .	

Question 5 (e)

Energy Diagram for a Two-Step Reaction



- Reactants \rightarrow transition state \rightarrow intermediate
- Intermediate \rightarrow transition state \rightarrow product

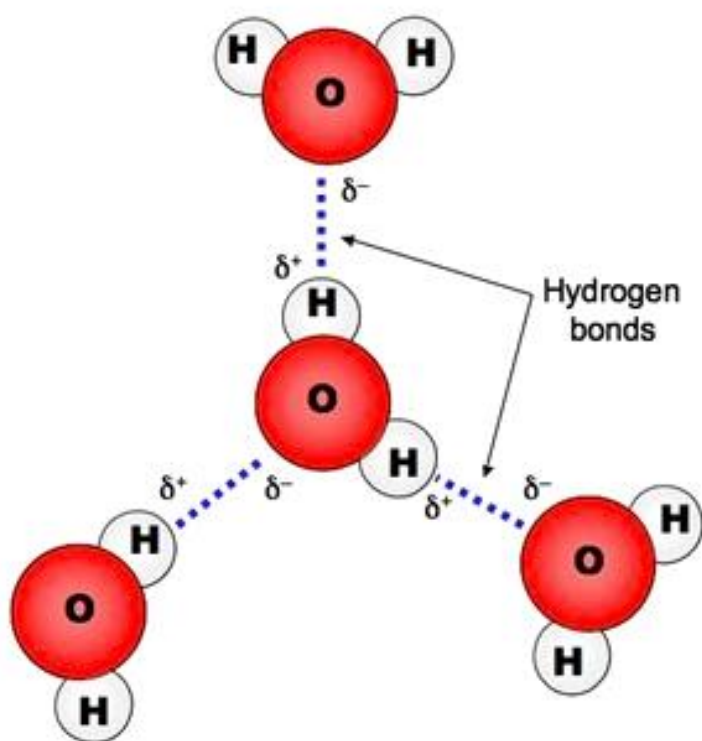
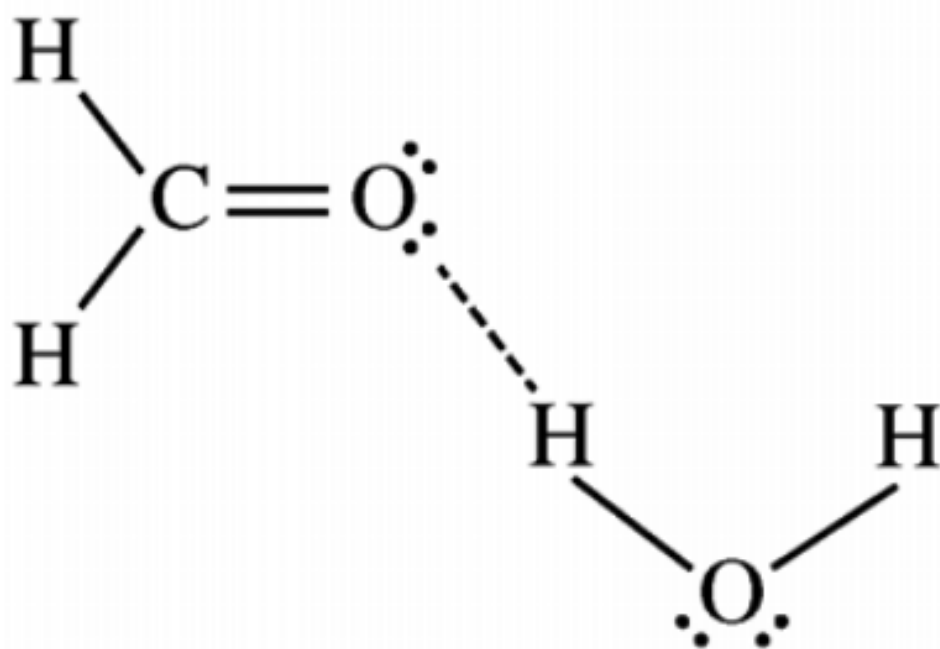


Question 6 (c)

CH_2Cl_2 is polar, whereas CCl_4 is not. Therefore, CH_2Cl_2 interacts with H_2O via dipole-dipole forces, while CCl_4 only interacts with water via dipole/induced dipole forces or LDFs, which would be weaker. As a result, CH_2Cl_2 has a greater solubility.

Question 6 (e)

- hydrogen bonding



Question 3

Which of the following correctly identifies which has the higher first-ionization energy, Cl or Ar, and supplies the best justification?

- (A) Cl, because of its higher electronegativity
- (B) Cl, because of its higher electron affinity
- (C) Ar, because of its completely filled valence shell
- (D) Ar, because of its higher effective nuclear charge

The first ionization energy varies in a predictable way across the periodic table. The ionization energy *decreases from top to bottom in groups*, and *increases from left to right across a period*. Thus, helium has the largest first ionization energy, while francium has one of the lowest.

- From top to bottom in a group, orbitals corresponding to higher values of the principal quantum number (n) are being added, which are on average further away from the nucleus. Since the outermost electrons are further away, they are less strongly attracted by the nucleus, and are easier to remove, corresponding to a lower value for the first ionization energy.
- From left to right across a period, more protons are being added to the nucleus, but the number of electrons in the inner, lower-energy shells remains the same. The valence electrons feel a higher effective nuclear charge — the sum of the charges on the protons in the nucleus and the charges on the inner, core electrons. The valence electrons are therefore held more tightly, the atom decreases in size (see [atomic radius](#)), and it becomes increasingly difficult to remove them, corresponding to a higher value for the first ionization energy.

Question 4

- Sealed rigid vessel = constant volume

There are two cases on which equilibrium depends. These are:

- **Addition of an inert gas at constant volume:**

When an inert gas is added to the system in equilibrium at constant volume, the total pressure will increase. But the concentrations of the products and reactants (i.e. ratio of their moles to the volume of the container) will not change.

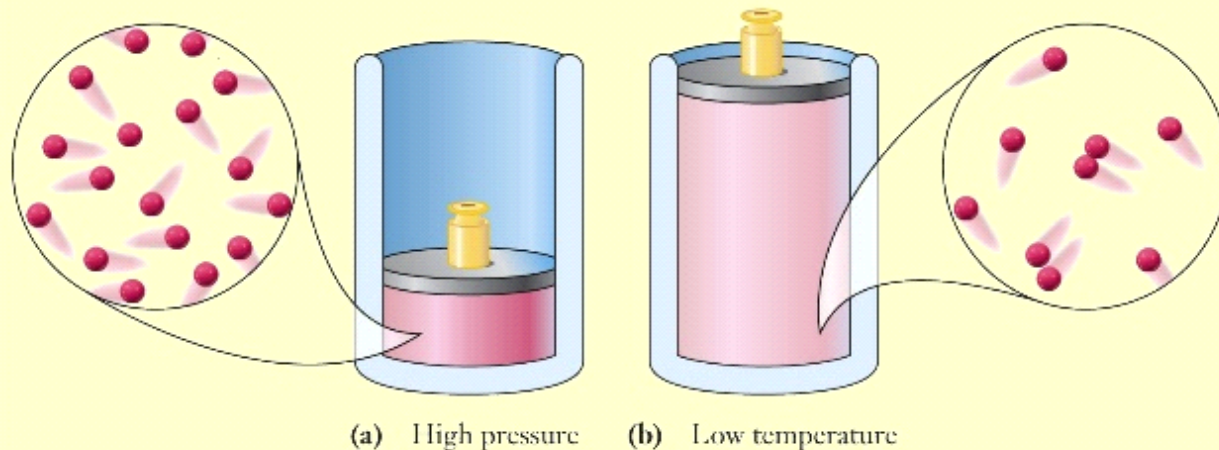
Hence, when an inert gas is added to the system in equilibrium at constant volume there will be no effect on the equilibrium.

- **Addition of an inert gas at constant pressure:**

When an inert gas is added to the system in equilibrium at constant pressure, then the total volume will increase. Hence, the number of moles per unit volume of various reactants and products will decrease. Hence, the equilibrium will shift towards the direction in which there is increase in number of moles of gases.

Question 6

Real Gases and Limitations of the Kinetic Theory

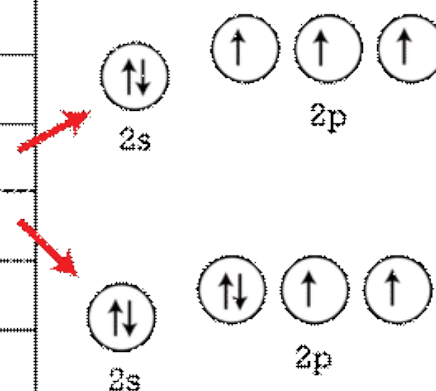


- The ideal gas model breaks down at high pressures and low temperatures.
 - high pressure: volume of particles no longer negligible
 - low temperature: particles move slowly enough to interact

43

Question 12

Element	Electron Configuration	Ionization Energy
Lithium (Li)	[He] $2s^1$	520 kJ/mol
Beryllium (Be)	[He] $2s^2$	899 kJ/mol
Boron (B)	[He] $2s^2 2p^1$	801 kJ/mol
Carbon (C)	[He] $2s^2 2p^2$	1086 kJ/mol
Nitrogen (N)	[He] $2s^2 2p^3$	1400 kJ/mol
Oxygen (O)	[He] $2s^2 2p^4$	1314 kJ/mol
Fluorine (F)	[He] $2s^2 2p^5$	1680 kJ/mol
Neon (Ne)	[He] $2s^2 2p^6$	2081 kJ/mol



Why the drop between groups 5 and 6 (N-O and P-S)?

Once again, you might expect the ionisation energy of the group 6 element to be higher than that of group 5 because of the extra proton. What is offsetting it this time?

N $1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$ 1st I.E. = 1400 kJ mol⁻¹

O $1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$ 1st I.E. = 1310 kJ mol⁻¹

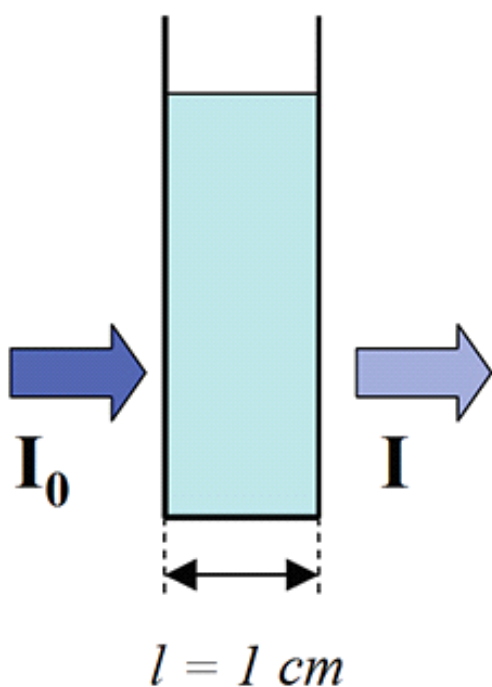
The screening is identical (from the $1s^2$ and, to some extent, from the $2s^2$ electrons), and the electron is being removed from an identical orbital.

The difference is that in the oxygen case the electron being removed is one of the $2p_x^2$ pair. The repulsion between the two electrons in the same orbital means that the electron is easier to remove than it would otherwise be.

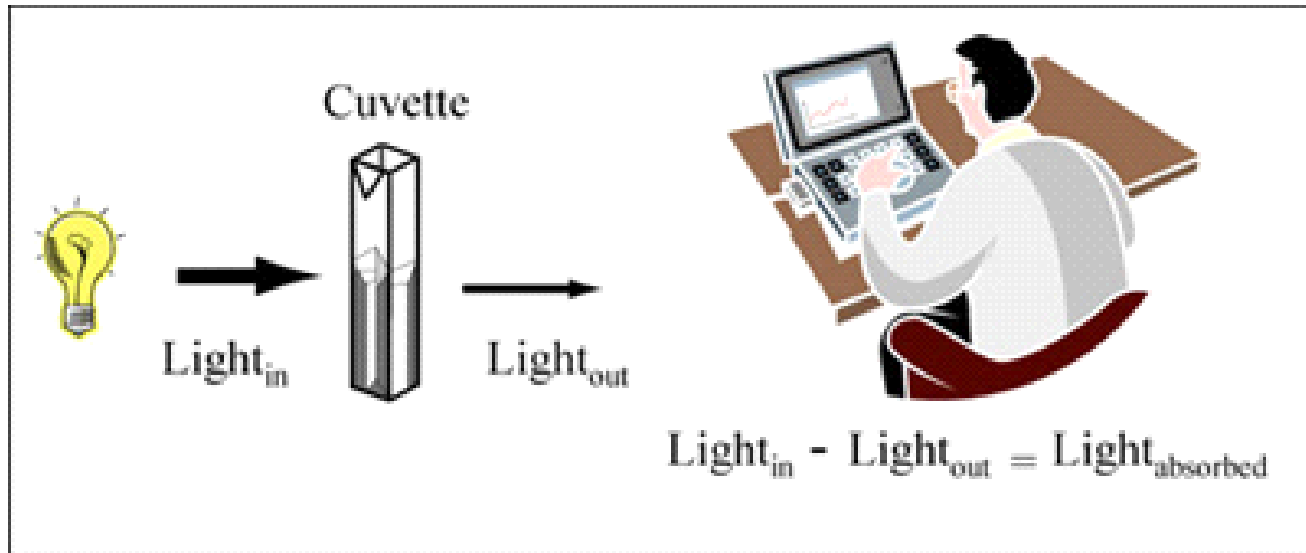
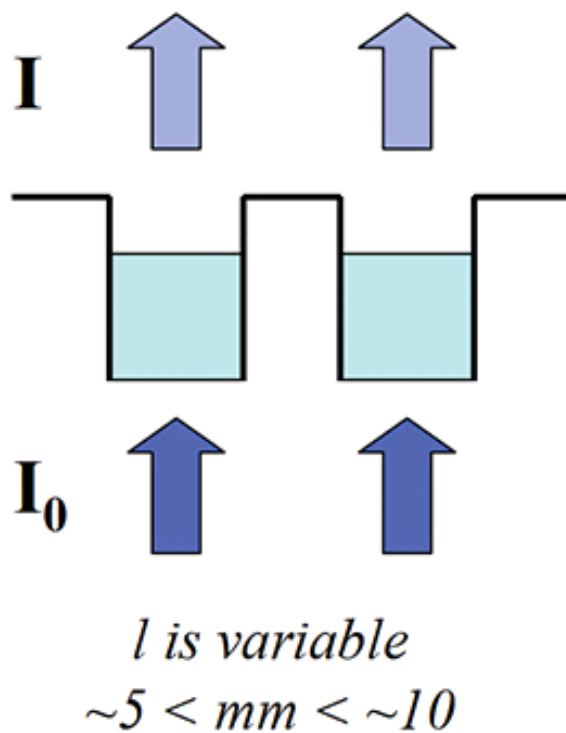
The drop in ionisation energy at sulphur is accounted for in the same way.

Question 27

Cuvette

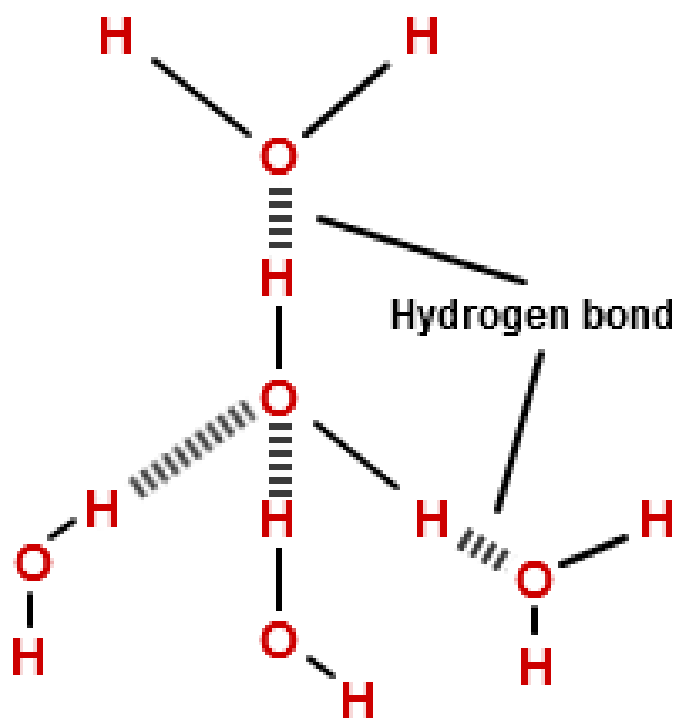


Microplate (96- or 384-well)

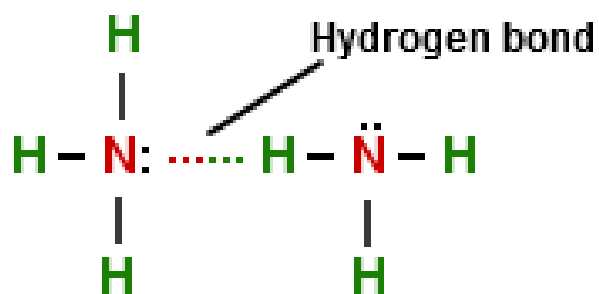


Question 30

- Common Hydrogen bonds: H-O, H-N



Water molecule



Ammonia molecule

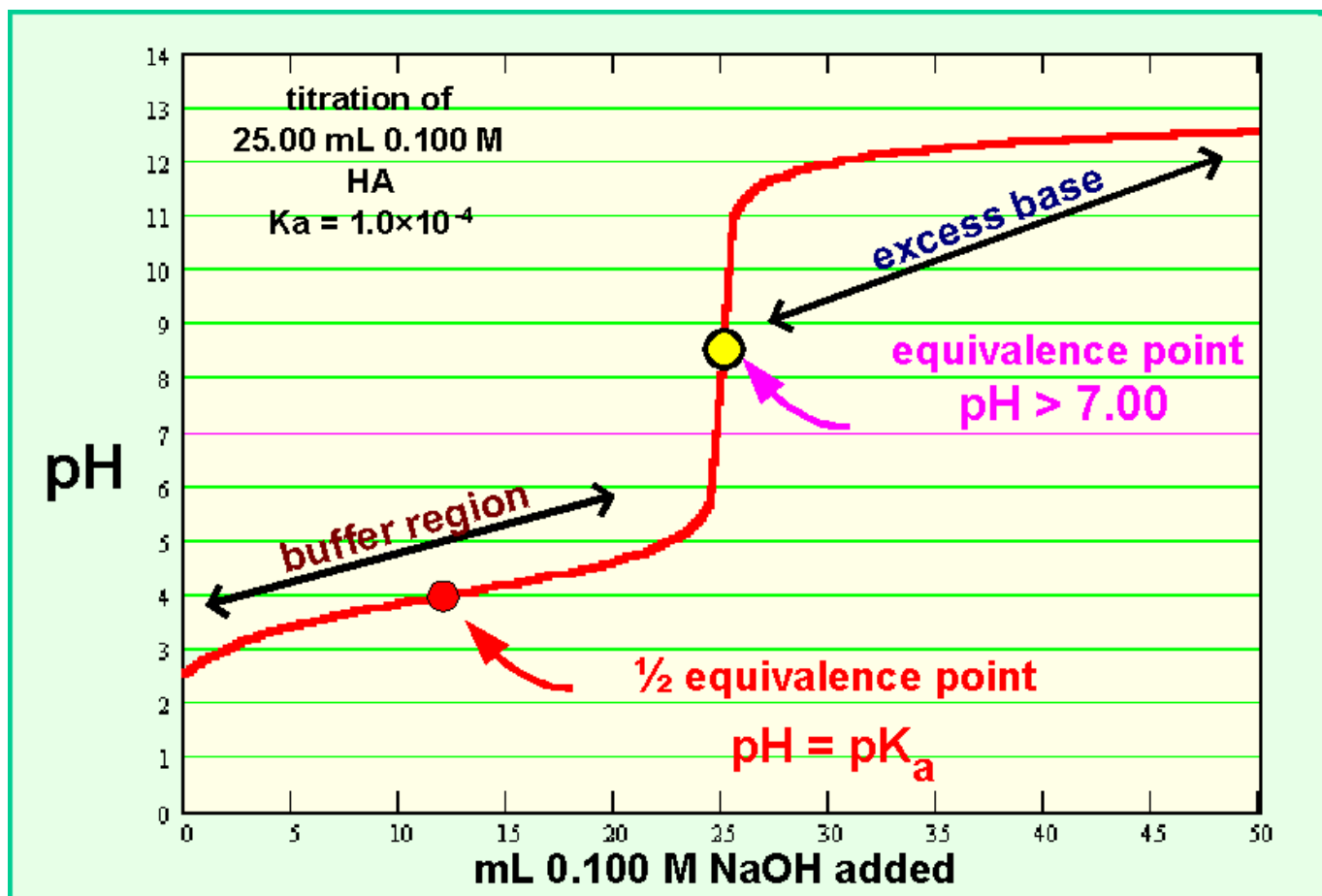
element	Donors	Donor strength	Acceptors	Acceptor strength
fluorine	F-H	very strong	F⁻ , F-H	very strong strong
oxygen	O-H (in an acid)	strong	O⁻-P , O⁻-S⁻ , O⁻-C ,	strong strong
oxygen	O-H (in water, or alcohols)	medium	O=P , O=S , O=C , H₂O , H-O-C , C-O-C	medium-strong medium
nitrogen	N⁺-H	strong	C=N-C	medium
nitrogen	N-H	medium	N(R)₃ ,	medium
sulfur	S-H	weak	S=C	medium-weak
carbon	C-H	weak	π -electrons	weak

Question 38

Because of the incomplete dissociation of the acid, the reaction is in equilibrium, with an acid dissociation constant, K_a , which is specific to that acid. **point** are the same. Therefore, at the **half-equivalence point**, the pH is equal to the **pKa**.

Experiment 6 Titration II

www.uccs.edu/Documents/chemistry/nsf/106%20Expt6V-Titration2.pdf



Question 40

Which of the following best explains why more energy is required for the process occurring at 110 K than for the process occurring at 90 K ?


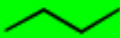

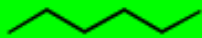




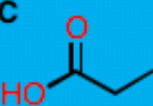
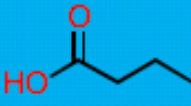
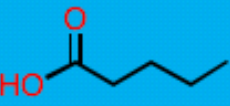
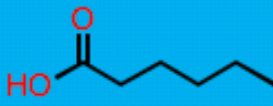


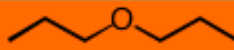
- (A) Intermolecular attractions are completely overcome during vaporization.
- (B) Intermolecular attractions in the solid phase are weaker than in the liquid phase.
- (C) Electron clouds of methane molecules are less polarizable at lower temperatures.
- (D) Vaporization involves a large increase in temperature.

Question 49

Trend #2 – For molecules with a given functional group, boiling point increases with molecular weight.

Look at the dramatic increases in boiling points as you increase molecular weight in all of these series:

In a given series, boiling point increases with molecular weight. **Why?**

ALKANES				
Boiling point	-42 °C	0 °C	36 °C	69 °C
ALCOHOLS				
Boiling point	97 °C	117 °C	138 °C	158 °C
CARBOXYLIC ACIDS				
Boiling point	141 °C	164 °C	186 °C	202 °C
ETHERS				
Boiling point	-24 °C	35 °C	89 °C	

Increasing surface area gives rise to increased Van Der Waals interactions

Here's the question: **How**, exactly do intermolecular forces increase as molecular weight increases?

Well, the key force that is acting here are Van der Waals dispersion forces, which are **proportional to surface area**. So as you increase the length of the chain, you also increase the surface area, which means that you increase the ability of individual molecules to attract each other.

2014 Free Response

Thursday, April 6, 2017

8:42 PM

Question 1 (a)

(ii) explain why the reaction is **best** represented by a net-ionic equation.

The net-ionic equation **shows the formation of the** $\text{PbI}_2(s)$ from $\text{Pb}^{2+}(aq)$ and $\text{I}^{-}(aq)$ ions, **omitting the** non-reacting species **(spectator ions)**, $\text{K}^{+}(aq)$ and $\text{NO}_3^{-}(aq)$.

1 point is earned for a valid explanation.

Question 2 (a)

(a) Identify a Brønsted-Lowry **conjugate acid-base pair** in the reaction. Clearly label which is the acid and which is the base.

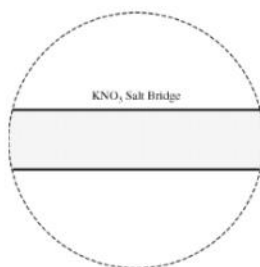
$\text{CH}_3\text{CH}_2\text{COOH}$ and $\text{CH}_3\text{CH}_2\text{COO}^{-}$
acid *base*

OR

H_3O^{+} and H_2O
acid *base*

1 point is earned for writing (or naming) either of the Brønsted-Lowry conjugate acid-base pairs with a clear indication of which is the acid and which is the base.

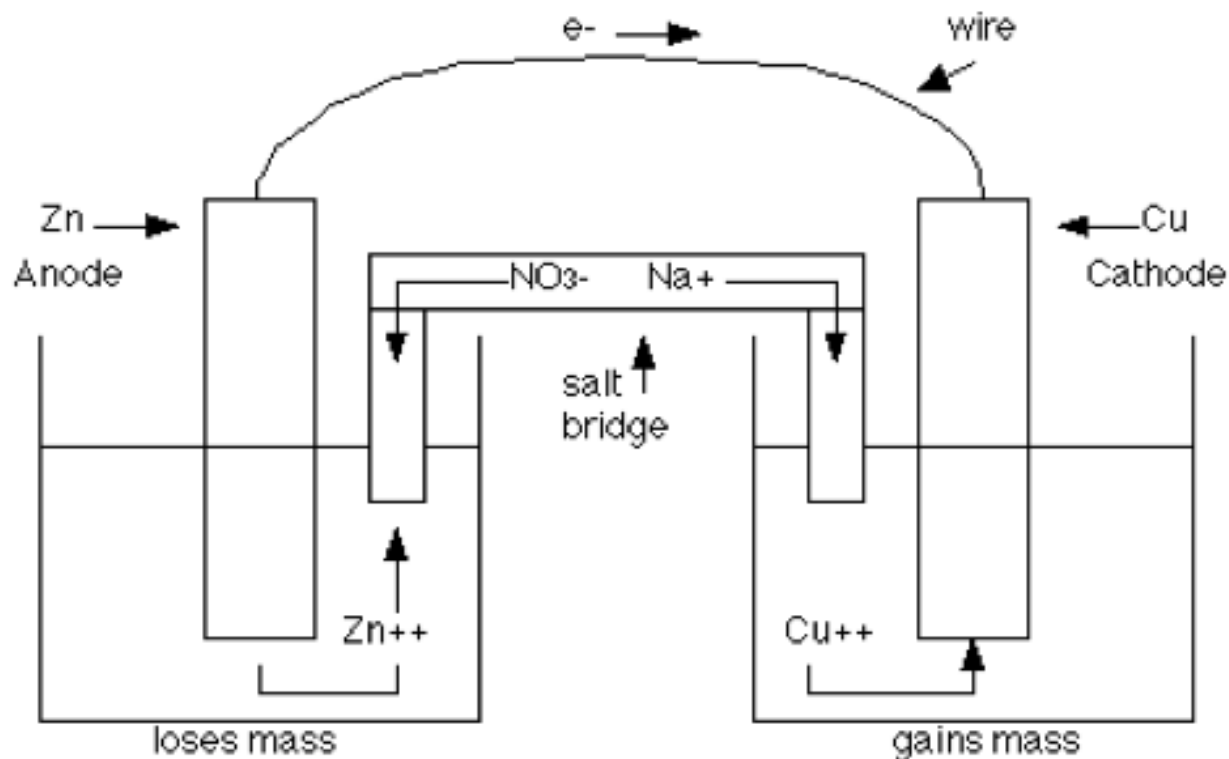
Question 3 (c)



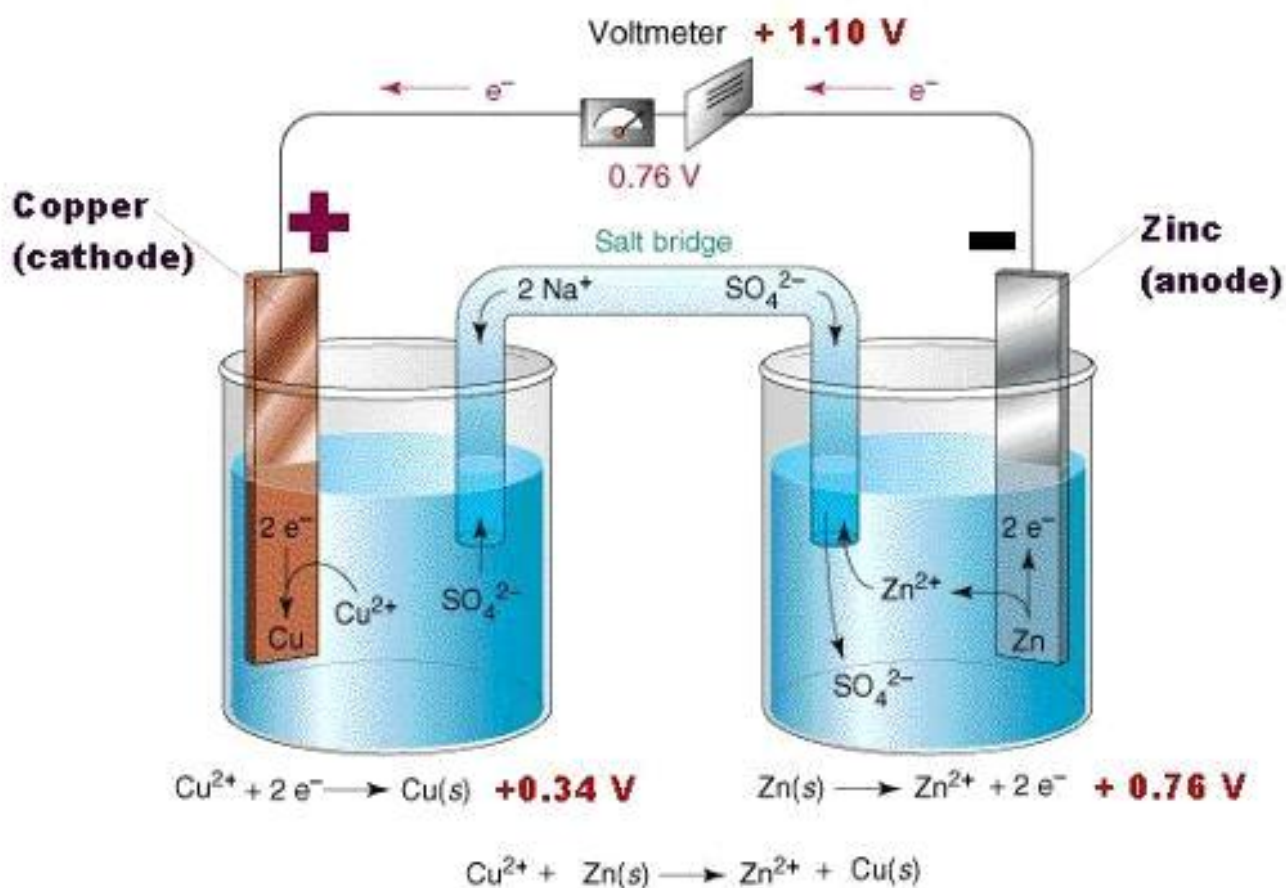
The response should show at least one K^{+} ion moving toward the Cu compartment on the left and at least one NO_3^{-} ion moving in the **opposite direction**.

1 point is earned for correct representation of both K^{+} and NO_3^{-} ions. (Including free electrons loses this point.)

1 point is earned for correctly indicating the direction of movement of both ions.



An electrochemical cell of the reaction:
 $\text{Zn(s)} + \text{Cu}^{++}(\text{aq}) \longrightarrow \text{Zn}^{++}(\text{aq}) + \text{Cu(s)}$



Question 3 (e)

(ii) Calculate the value of ΔG° for the reaction. Include units with your answer.

$\Delta G^\circ = -nFE^\circ$ $\Delta G^\circ = -\frac{2 \text{ mol } e^-}{\text{mol}_{rxn}} \times \frac{96,485 \text{ C}}{\text{mol } e^-} \times \frac{0.48 \text{ J}}{\text{C}} = -93,000 \text{ J/mol}_{rxn} = -93 \text{ kJ/mol}_{rxn}$	<p>1 point is earned for the correct number of electrons.</p> <p>1 point is earned for the correct answer with unit.</p>
---	--

Nernst Equation

- Hydro-electrometallurgical processes often involve electrochemical reactions.
- For electrochemical reaction

$$\Delta G = -nFE, \quad \Delta G^\circ = -nFE^\circ, \text{ therefore}$$

$$E = E^\circ - \frac{RT}{nF} \ln K \quad \leftarrow \text{Nernst Equation}$$

In which,

E = potential for reduction-oxidation reaction

E° = standard potential for reduction-oxidation reaction

n = number of electron involved in the electrochemical reaction,

F = Faraday constant = 96485 Coulomb/mole of electron

- Spontaneous process $\rightarrow E > 0 \rightarrow \Delta G < 0$

Question 4 (c)

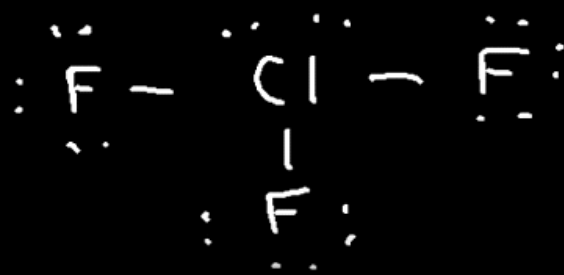
- (c) After 20 minutes some $\text{CO}_2(g)$ was injected into the container, initially raising the pressure to 1.5 atm. Would the final pressure inside the container be less than, greater than, or equal to 1.04 atm? Explain your reasoning.

<p>The final pressure would be equal to 1.04 atm. Equilibrium was reached in both experiments; the equilibrium pressure at this temperature is 1.04 atm. As the reaction shifts toward the reactant, the amount of $\text{CO}_2(g)$ in the container will decrease until the pressure returns to 1.04 atm.</p>	<p>1 point is earned for the correct answer with justification.</p>
---	---

Question 5 (b)

ClF_3 Chlorine Trifluoride

$$7 + 7(3) = 28 - 24 = 4$$

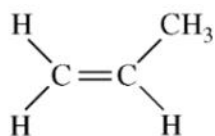


T-shaped

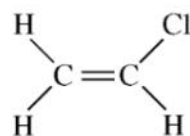


Charge Formal	=	Valence Electrons	-	NonBonding Val Electrons	-	$\frac{\text{Bonding Electrons}}{2}$	
Cl	=	7	-	4	-	$6/2$	= 0
F	=	7	-	6	-	$2/2$	= 0

Question 6 (b)



Propene



Vinyl Chloride (chloroethene)

- (b) The boiling point of liquid propene (226 K) is lower than the boiling point of liquid vinyl chloride (260 K). Account for this difference in terms of the types and strengths of intermolecular forces present in each liquid.

Both substances have dipole-dipole interactions and London dispersion forces (or propene is essentially nonpolar with only LDFs while vinyl chloride has both LDFs and dipole-dipole forces). Propene contains a CH_3 group, but vinyl chloride contains a Cl atom. Vinyl chloride thus has a larger electron cloud, is more polarizable, and has a larger dipole moment. Thus intermolecular attractions are stronger in vinyl chloride, which results in it having the higher boiling point.

1 point is earned for a discussion of intermolecular forces and for a comparison of their relative strengths.

Question 7 (a)

Trial Number	Initial $P_{\text{cis-2-butene}}$ (torr)	V (L)	T (K)	$t_{1/2}$ (s)
1	300.	2.00	350.	100.
2	600.	2.00	350.	100.
3	300.	4.00	350.	100.
4	300.	2.00	365	50.

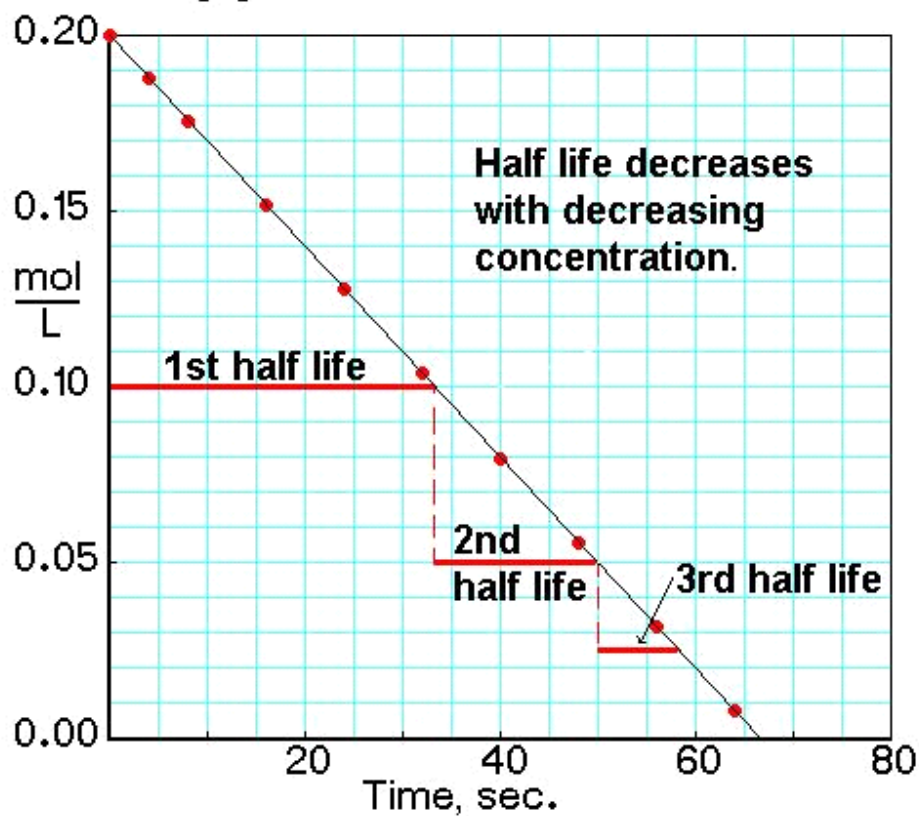
- (a) The reaction is first order. Explain how the data in the table are consistent with a first-order reaction.

For a first-order reaction, the half-life is independent of reactant concentration (or pressure) at constant T , as shown in trials 1, 2, and 3.

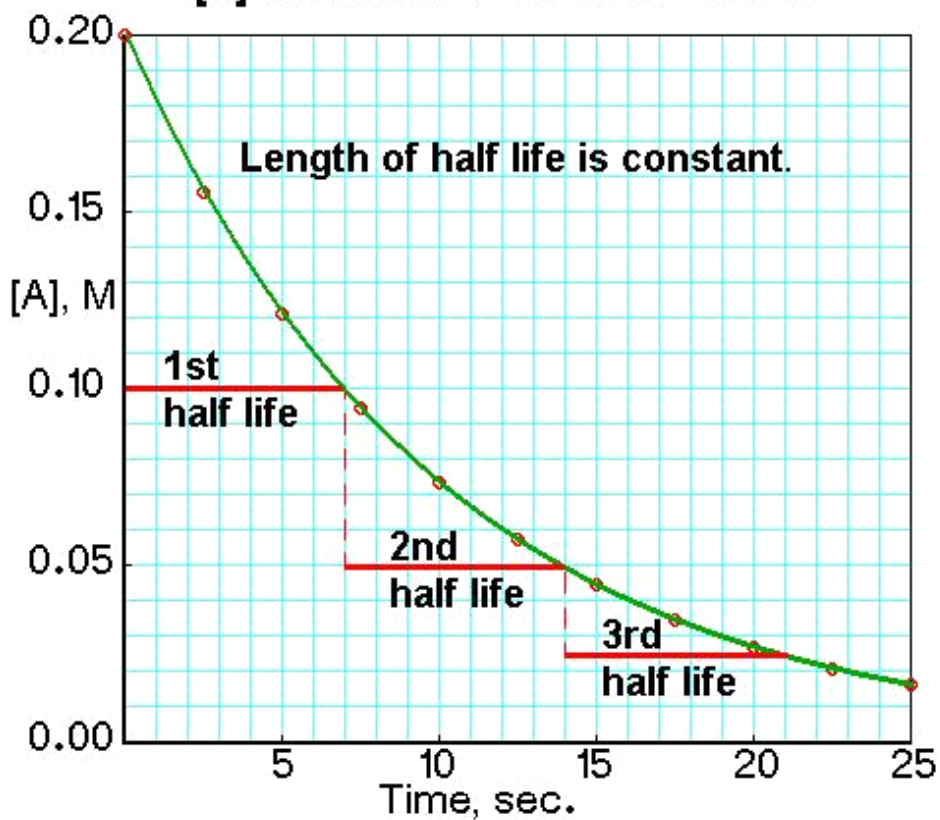
1 point is earned for a correct explanation.

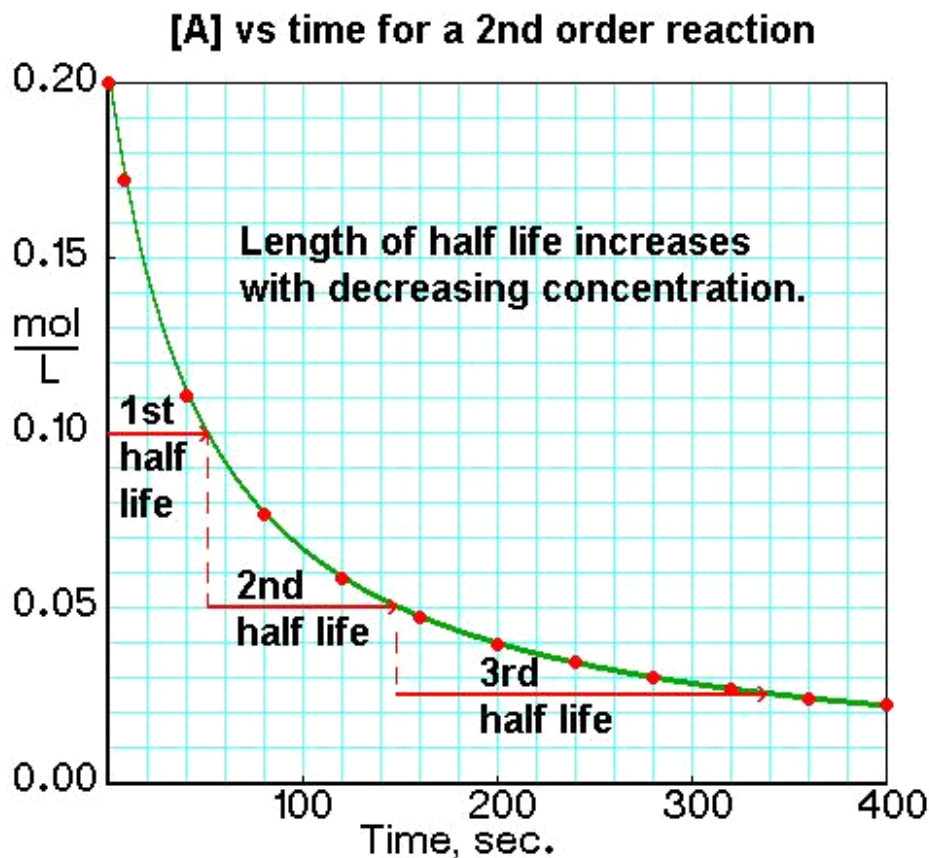
Order	Rate Law	Concentration - Time Equation	Half Life	Graphical Plot
0	Rate = k_0	$[A]_0 - [A] = k_0 t$	$\frac{[A]_0}{2k_0}$	$[A]$ vs t
1	Rate = $k_1[A]$	$\log \frac{[A]_0}{[A]} = \frac{k t}{2.303}$	$\frac{0.693}{k}$	$\log A$ vs t
2	Rate = $k_2[A]^2$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$	$\frac{1}{(k_2 [A]_0)}$	$\frac{1}{[A]}$ vs t

[A] vs time for a 0 order reaction



[A] vs time for a 1st order reaction





Half-Life

The **half-life** of a reaction, $t_{1/2}$, is the time required for the concentration of a reactant to reach half its initial value, $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$. Half-life is a convenient way to describe how fast a reaction occurs, especially if it is a first-order process. A fast reaction has a short half-life.

We can determine the half-life of a first-order reaction by substituting $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$ for $[A]_t$ and $t_{1/2}$ for t in Equation 14.12:

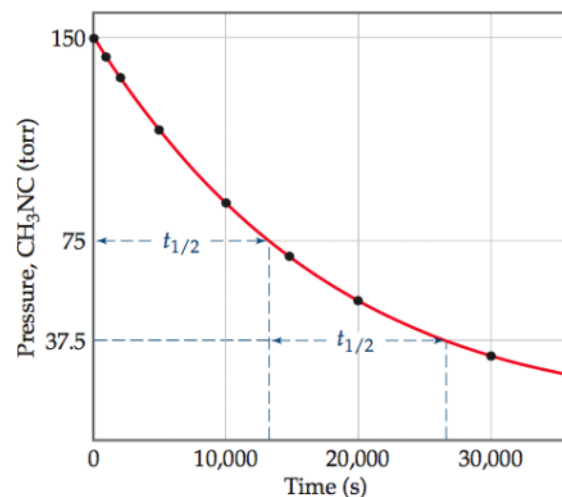
$$\begin{aligned}\ln \frac{\frac{1}{2}[A]_0}{[A]_0} &= -kt_{1/2} \\ \ln \frac{1}{2} &= -kt_{1/2} \\ t_{1/2} &= -\frac{\ln \frac{1}{2}}{k} = \frac{0.693}{k} \quad [14.15]\end{aligned}$$

From Equation 14.15, we see that $t_{1/2}$ for a first-order rate law does not depend on the initial concentration of any reactant. Consequently, the half-life remains constant throughout the reaction. If, for example, the concentration of a reactant is 0.120 M at some instant in the reaction, it will be $\frac{1}{2}(0.120 \text{ M}) = 0.060 \text{ M}$ after one half-life. After one more half-life passes, the concentration will drop to 0.030 M, and so on. Equation 14.15 also indicates that, for a first-order reaction, we can calculate $t_{1/2}$ if we know k and calculate k if we know $t_{1/2}$.

The change in concentration over time for the first-order rearrangement of gaseous methyl isonitrile at 199 °C is graphed in ► **Figure 14.11**. Because the concentration of this gas is directly proportional to its pressure during the reaction, we have chosen to plot pressure rather than concentration in this graph. The first half-life occurs at 13,600 s (3.78 h). At a time 13,600 s later, the methyl isonitrile pressure (and therefore, concentration) has decreased to half of one-half, or one-fourth, of the initial value. In a first-order reaction, the concentration of the reactant decreases by one-half in each of a series of regularly spaced time intervals, each interval equal to $t_{1/2}$.



► **Figure 14.10** Comparison of first-order and zero-order reactions for the disappearance of reactant A with time.



► **Figure 14.11** Kinetic data for the rearrangement of methyl isonitrile to acetonitrile at 199 °C, showing the half-life of the reaction.

The half-life for second-order and other reactions depends on reactant concentrations and therefore changes as the reaction progresses. We obtained Equation 14.15 for the half-life for a first-order reaction by substituting $[A]_{t_{1/2}} = \frac{1}{2}[A]_0$ for $[A]_t$ and $t_{1/2}$ for t in Equation 14.12. We find the half-life of a second-order reaction by making the same substitutions into Equation 14.14:

$$\begin{aligned}\frac{1}{\frac{1}{2}[A]_0} &= kt_{1/2} + \frac{1}{[A]_0} \\ \frac{2}{[A]_0} - \frac{1}{[A]_0} &= kt_{1/2} \\ t_{1/2} &= \frac{1}{k[A]_0}\end{aligned}\quad [14.17]$$

In this case, the half-life depends on the initial concentration of reactant—the lower the initial concentration, the longer the half-life.

Question 7 (c)

- (c) Is the initial rate of the reaction in trial 1 greater than, less than, or equal to the initial rate in trial 2 ? Justify your answer.

<p>The initial rate in trial 1 is less than that in trial 2 because $\text{rate} = k[\text{cis-2-butene}]$ or $\text{rate} = kP_{\text{cis-2-butene}}$ (with reference to values from both trials).</p> <p>OR</p> <p>because the initial concentration of <i>cis</i>-2-butene in trial 1 is less than that in trial 2 and k is constant.</p>	<p>1 point is earned for the correct answer with justification.</p>
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Question 7 (d)

- (d) The half-life of the reaction in trial 4 is less than the half-life in trial 1. Explain why, in terms of activation energy.

<p>The temperature is higher in trial 4, meaning that the KE_{avg} of the molecules is greater. Consequently, in this trial a greater fraction of collisions <u>have sufficient energy to overcome the activation energy barrier</u>, thus the rate is greater.</p>	<p>1 point is earned for a correct answer with justification.</p>
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2015 Multiple Choice

Wednesday, April 19, 2017 12:35 AM

Question 16

In the reaction:



$$K_c = \frac{pC^c pD^d}{pA^a pB^b}$$

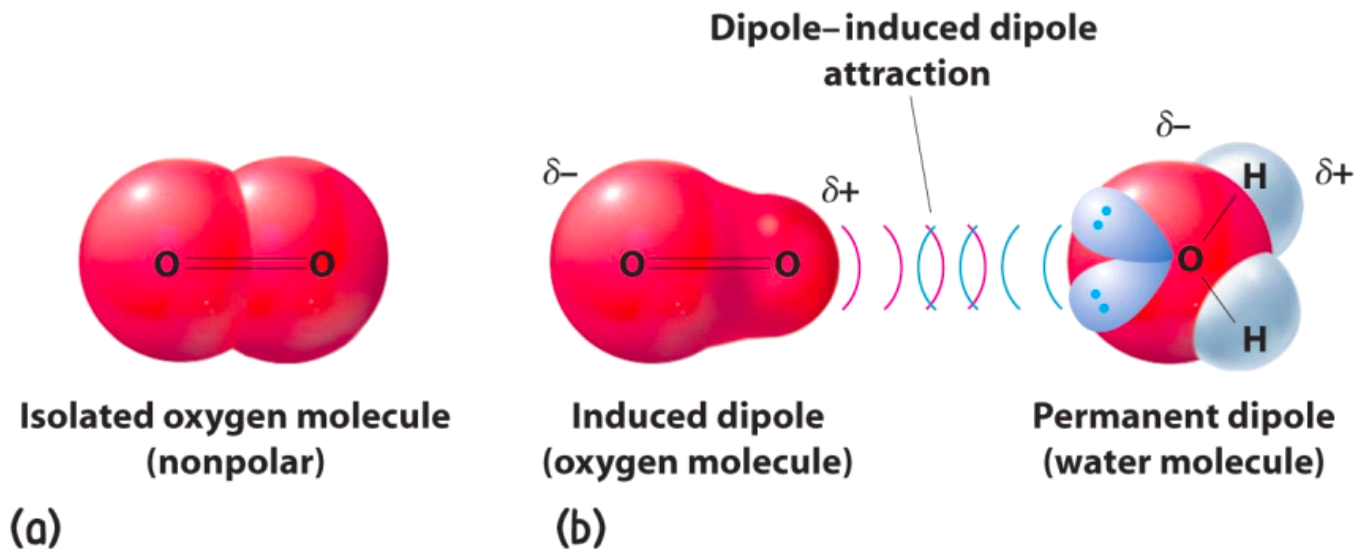
pA = partial pressure of A in kPa

a = number of moles of A

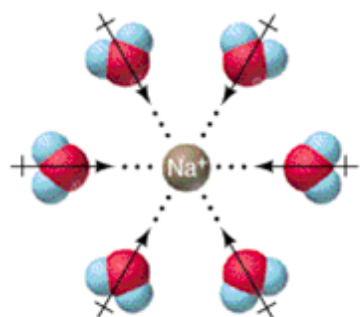
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Question 21

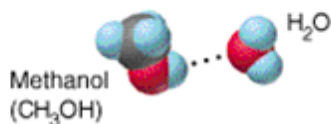
- Dipole-induced dipole interaction



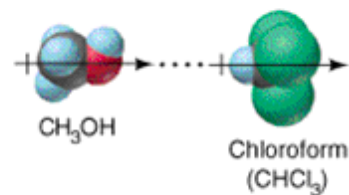
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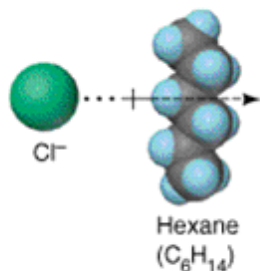
Ion-dipole



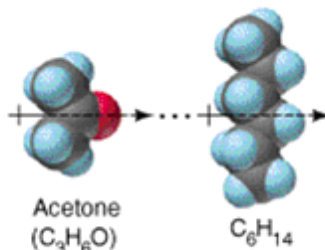
H bond



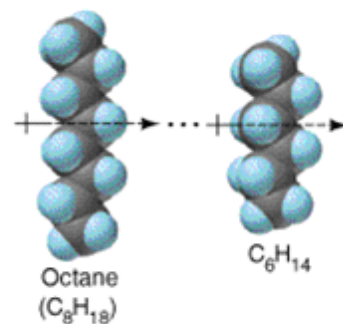
Dipole-dipole



Ion-induced dipole



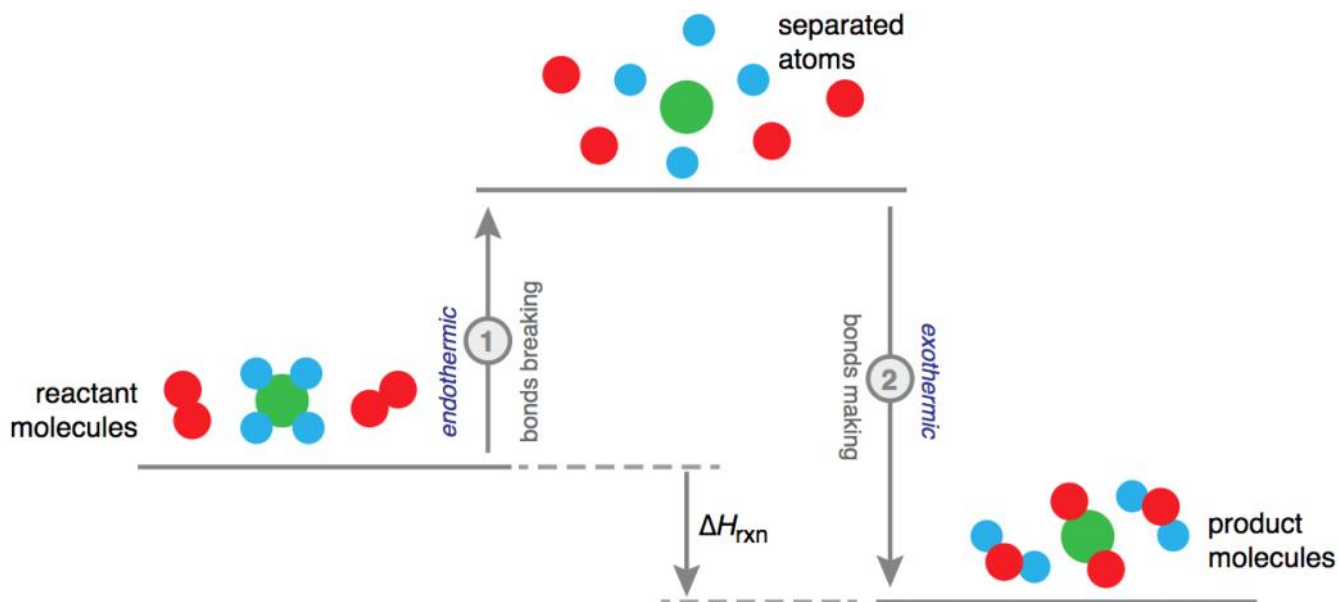
Dipole-induced dipole



Dispersion

Question 29

- ΔH° = bond enthalpies for the bonds broken - bond enthalpies for the bonds formed



Question 34

The Ion Product

Q is generally called the *ion product*.

$Q > K_{\text{sp}}$ Precipitation *should* occur.

$Q = K_{\text{sp}}$ The solution is *just* saturated.

$Q < K_{\text{sp}}$ Precipitation *cannot* occur.

Q_{sp} and K_{sp}

Q_{sp} is called the **ion-product expression** for a slightly soluble ionic compound.

For any slightly soluble compound M_pX_q , which consists of ions M^{n+} and X^{z-} ,

$$Q_{sp} = [M^{n+}]^p[X^{z-}]^q$$

When the solution is saturated, the system is at equilibrium, and $Q_{sp} = K_{sp}$, the **solubility product constant**.

The K_{sp} value of a salt indicates how far the dissolution proceeds at equilibrium (saturation).

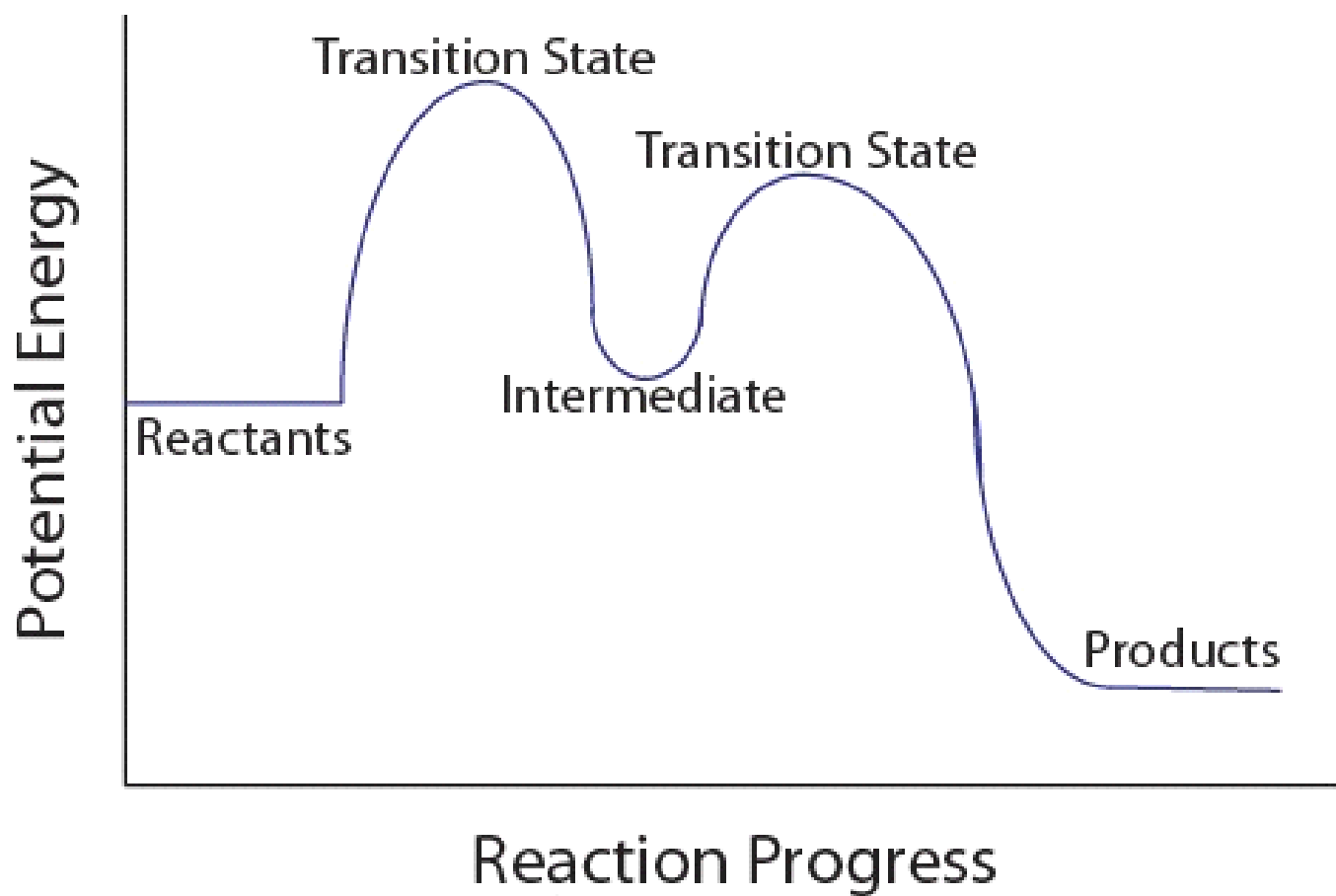


19-9



Question 43

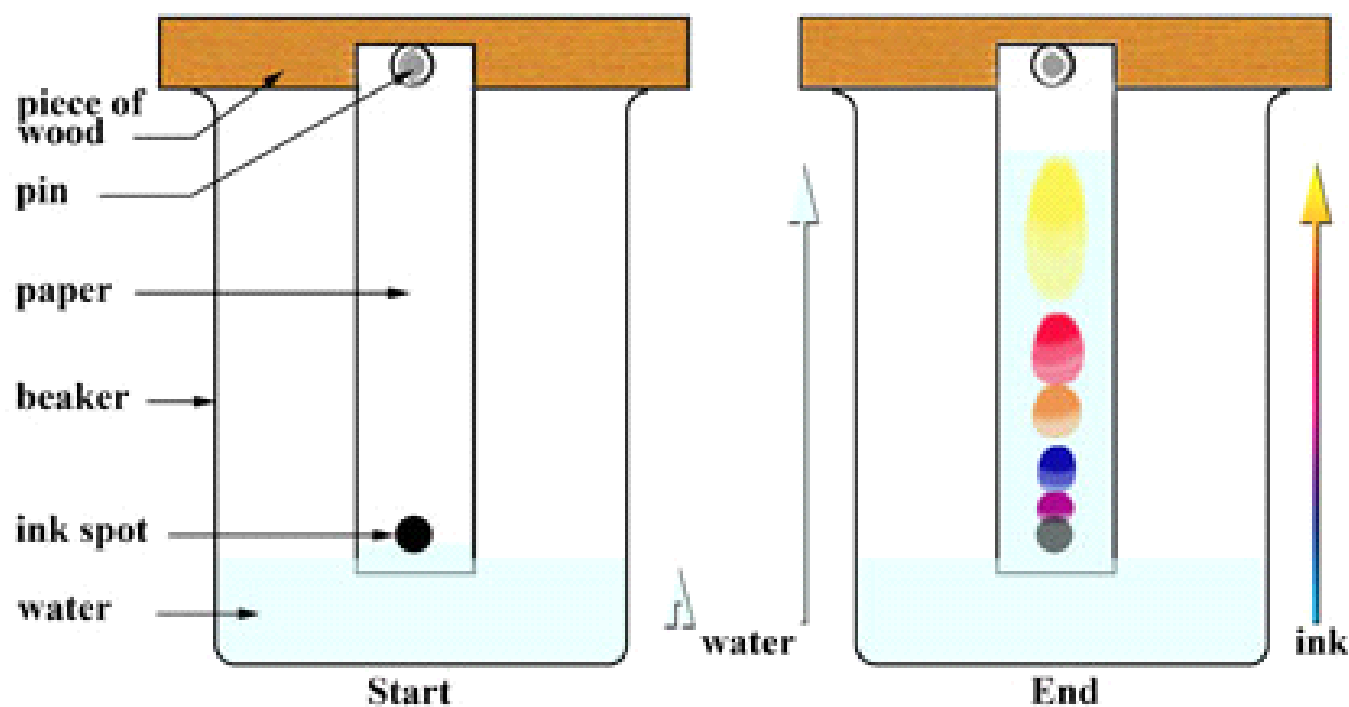
- Intermediate should not be lower than products



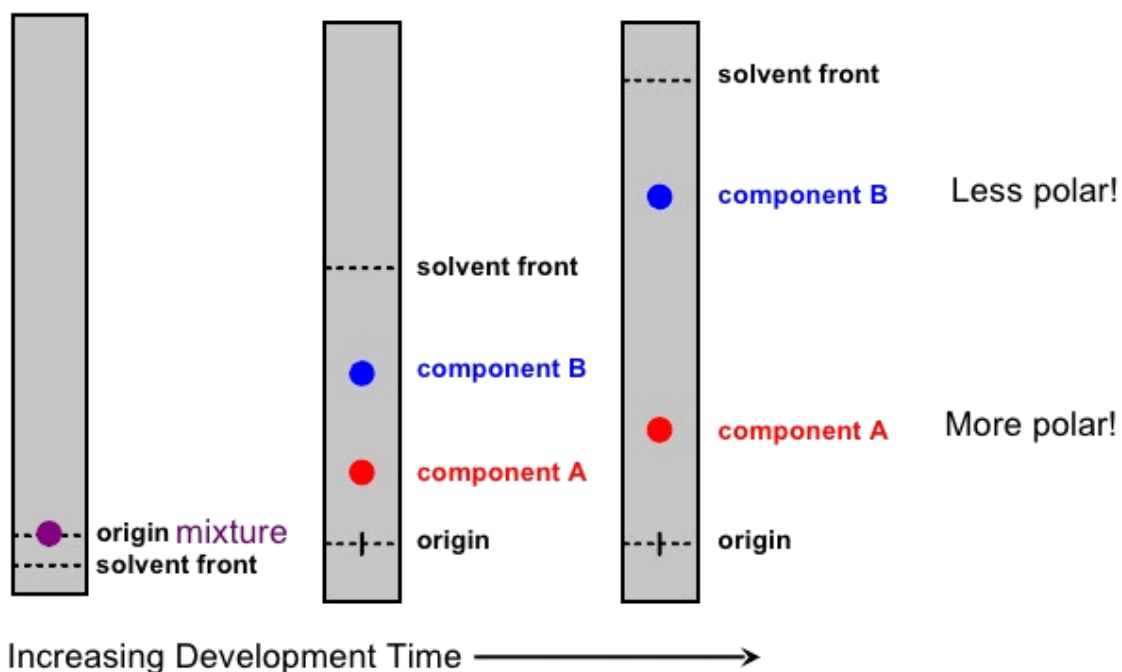
Question 49

- Chromatography Experiment

Simple chromatography



Thin-Layer Chromatography: A Two-Component Mixture



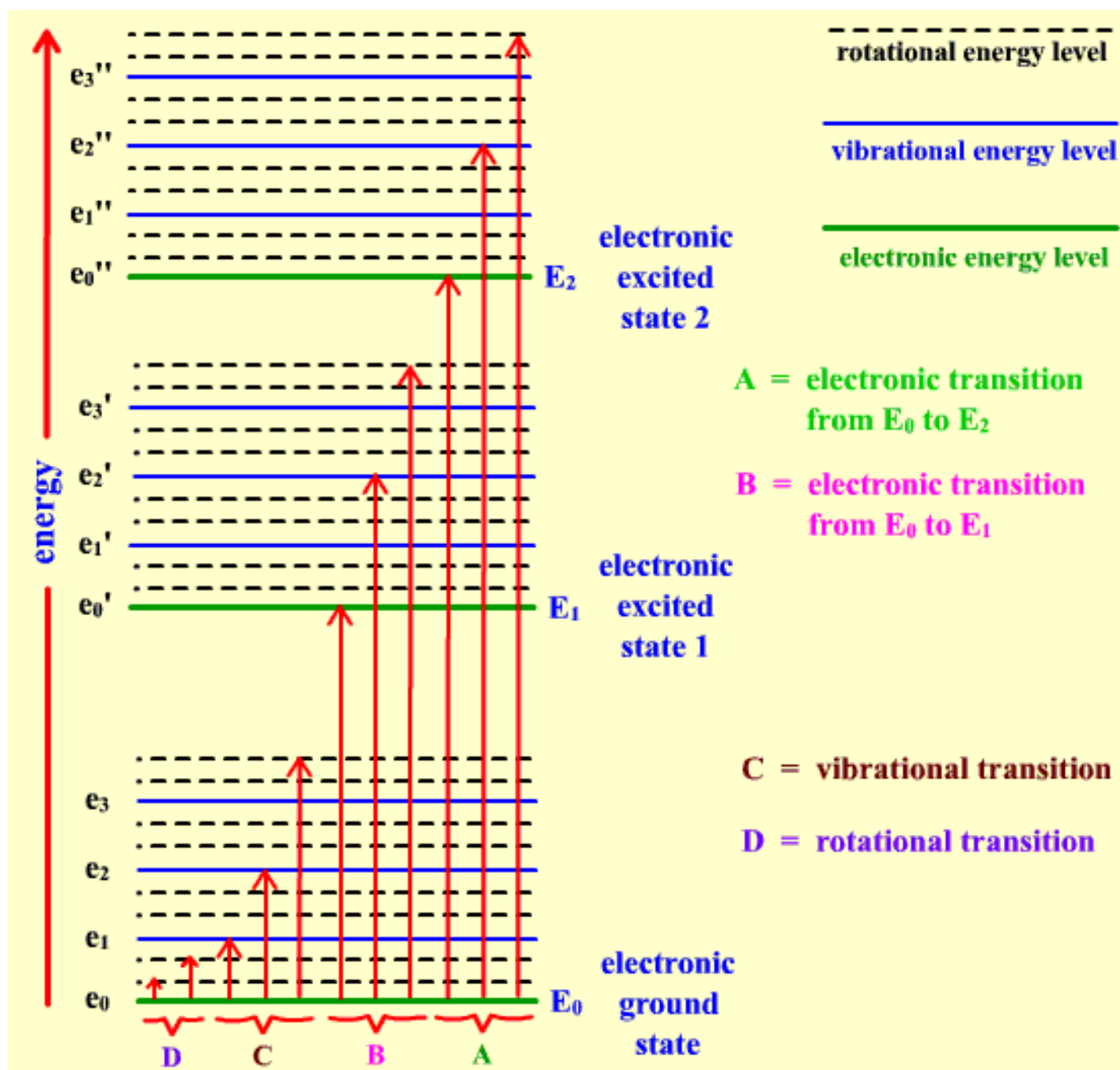
Rule of thumb:

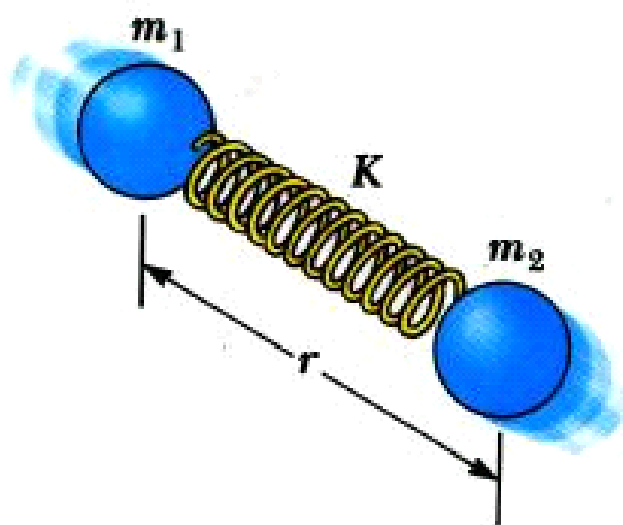
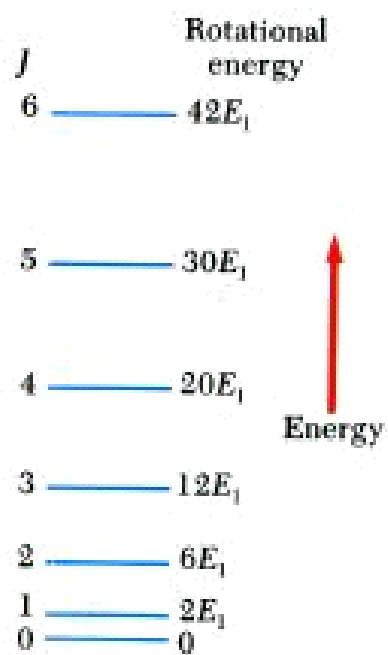
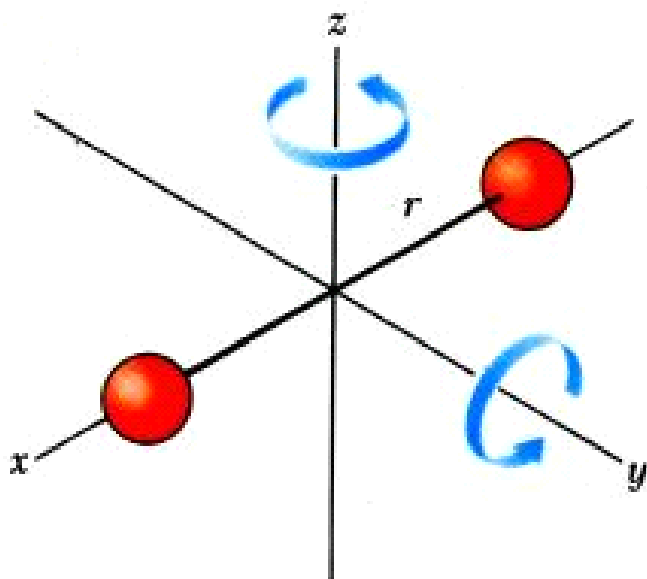
- The component that travels the least distance on the TLC plate is the most polar, since it binds to the silica most tightly.
- The component that travels the maximum distance is the least polar; it binds to the silica least tightly and is most soluble in the non-polar solvent (mobile phase), and hence moves up the plate with the solvent.

So just by looking at a TLC plate, you can tell which component is more polar and which component is less polar. There is also a quantitative parameter, termed as *retention factor* (R_f) that can be calculated for every individual component and this value is very commonly used in the 'world of chemical syntheses'. This value is invariably reported in manuscripts so that people who replicate the synthesis of a compound can verify that they too are getting the same R_f values for the same compounds.

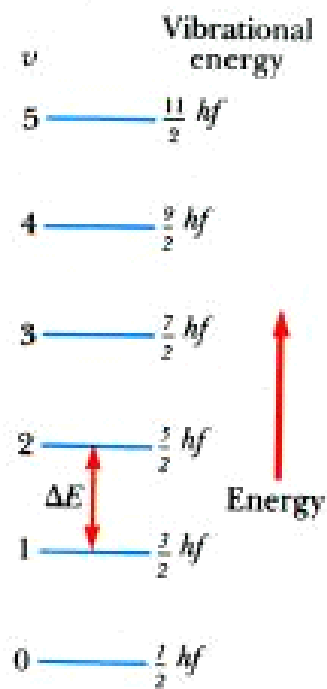
Question 50

- Electronic transition < Molecular vibration < Molecular rotation





(a)



(b)

2015 Free Response

Thursday, April 6, 2017 4:36 PM

Question 1 (c)

(c) The zinc-air cell is taken to the top of a mountain where the air pressure is lower.

(i) Will the cell potential be higher, lower, or the same as the cell potential at the lower elevation?

The cell potential will be lower.	1 point is earned for indicating a lower cell potential.
-----------------------------------	--

(ii) Justify your answer to part (c)(i) based on the equation for the overall cell reaction and the information above.

$O_2(g)$, a reactant in the cell reaction, will be at a lower partial pressure at the higher elevation; thus the reaction has a <u>greater value of Q (closer to K)</u> . Deviations in partial pressure that take the cell closer to equilibrium will decrease the magnitude of the cell potential.	1 point is earned for a justification that relates a lower pressure (or concentration) of $O_2(g)$ to Q , or a qualitative approach using the <u>Nernst equation</u> .
---	--

In electrochemistry, the **Nernst equation** is an **equation** that relates the reduction potential of an electrochemical reaction (half-cell or full cell reaction) to the standard electrode potential, temperature, and activities (often approximated by concentrations) of the chemical species undergoing reduction and oxidation ...

Nernst equation - Wikipedia

https://en.wikipedia.org/wiki/Nernst_equation

$$\begin{aligned} E &= E^0 + \frac{kT}{e} \ln \frac{[\text{Red}]}{[\text{Ox}]} \\ &= E^0 - \frac{RT}{F} \ln \frac{[\text{Ox}]}{[\text{Red}]} \end{aligned}$$

The Nernst Equation

The effect of concentration on cell emf can be obtained from the effect of concentration on free-energy change. [Section 19.7](#) Recall that the free-energy change for any chemical reaction, ΔG , is related to the standard free-energy change for the reaction, ΔG° :

$$\Delta G = \Delta G^\circ + RT \ln Q \quad [20.15]$$

The quantity Q is the reaction quotient, which has the form of the equilibrium-constant expression except that the concentrations are those that exist in the reaction mixture at a given moment. [Section 15.6](#)

Substituting $\Delta G = -nFE$ (Equation 20.11) into Equation 20.15 gives

$$-nFE = -nFE^\circ + RT \ln Q$$

Solving this equation for E gives the **Nernst equation**:

$$E = E^\circ - \frac{RT}{nF} \ln Q \quad [20.16]$$

This equation is customarily expressed in terms of the base-10 logarithm:

$$E = E^\circ - \frac{2.303 RT}{nF} \log Q \quad [20.17]$$

At $T = 298 \text{ K}$, the quantity $2.303 RT/F$ equals 0.0592 , with units of volts, and so the Nernst equation simplifies to

$$E = E^\circ - \frac{0.0592 \text{ V}}{n} \log Q \quad (T = 298 \text{ K}) \quad [20.18]$$

Question 2 (c)

Relationship between ΔG° and K

We can now use Equation 19.19 to derive the relationship between ΔG° and the equilibrium constant, K . At equilibrium, $\Delta G = 0$ and $Q = K$. Thus, at equilibrium, Equation 19.19 transforms as follows:

$$\begin{aligned} \Delta G &= \Delta G^\circ + RT \ln Q \\ 0 &= \Delta G^\circ + RT \ln K \\ \Delta G^\circ &= -RT \ln K \end{aligned} \quad [19.20]$$

Equation 19.20 is a very important one, with broad significance in chemistry. By relating K to ΔG° , we can also relate K to entropy and enthalpy changes for a reaction.

We can also solve Equation 19.20 for K , to yield an expression that allows us to calculate K if we know the value of ΔG° :

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

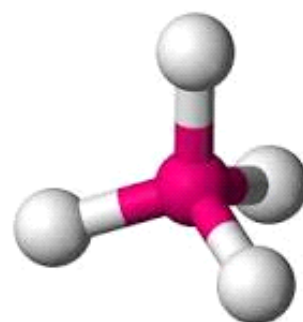
$$K = e^{-\Delta G^\circ/RT} \quad [19.21]$$

As usual, we must be careful in our choice of units. In Equations 19.20 and 19.21 we again express ΔG° in kJ/mol. In the equilibrium-constant expression, we use atmospheres for gas pressures, molarities for solutions; and solids, liquids, and solvents do not appear in the expression. ∞ (Section 15.4) Thus, the equilibrium constant is K_p for gas-phase reactions and K_c for reactions in solution. ∞ (Section 15.2)

From Equation 19.20 we see that if ΔG° is negative, $\ln K$ must be positive, which means $K > 1$. Therefore, the more negative ΔG° is, the larger K is. Conversely, if ΔG° is positive, $\ln K$ is negative, which means $K < 1$. Finally, if ΔG° is zero, $K = 1$.

Question 2 (e)

In a tetrahedral molecular geometry, a central atom is located at the center with four substituents that are located at the corners of a tetrahedron. The bond angles are $\cos^{-1}(-1/3) = 109.4712206...^\circ \approx 109.5^\circ$ when all four substituents are the same, as in methane (CH_4) as well as its heavier analogues.



Tetrahedral molecular geometry - Wikipedia

https://en.wikipedia.org/wiki/Tetrahedral_molecular_geometry

Question 2 (f)

- (f) During the dehydration experiment, $\text{C}_2\text{H}_4(g)$ and unreacted $\text{C}_2\text{H}_5\text{OH}(g)$ passed through the tube into the water. The C_2H_4 was quantitatively collected as a gas, but the unreacted $\text{C}_2\text{H}_5\text{OH}$ was not. Explain this observation in terms of the intermolecular forces between water and each of the two gases.

Ethene is only slightly soluble in water because the weak dipole/induced dipole intermolecular attractions between nonpolar ethene molecules and polar water molecules are weaker than the hydrogen bonds between water molecules. Ethanol molecules are soluble in water because they are polar and form hydrogen bonds with water molecules as they dissolve.

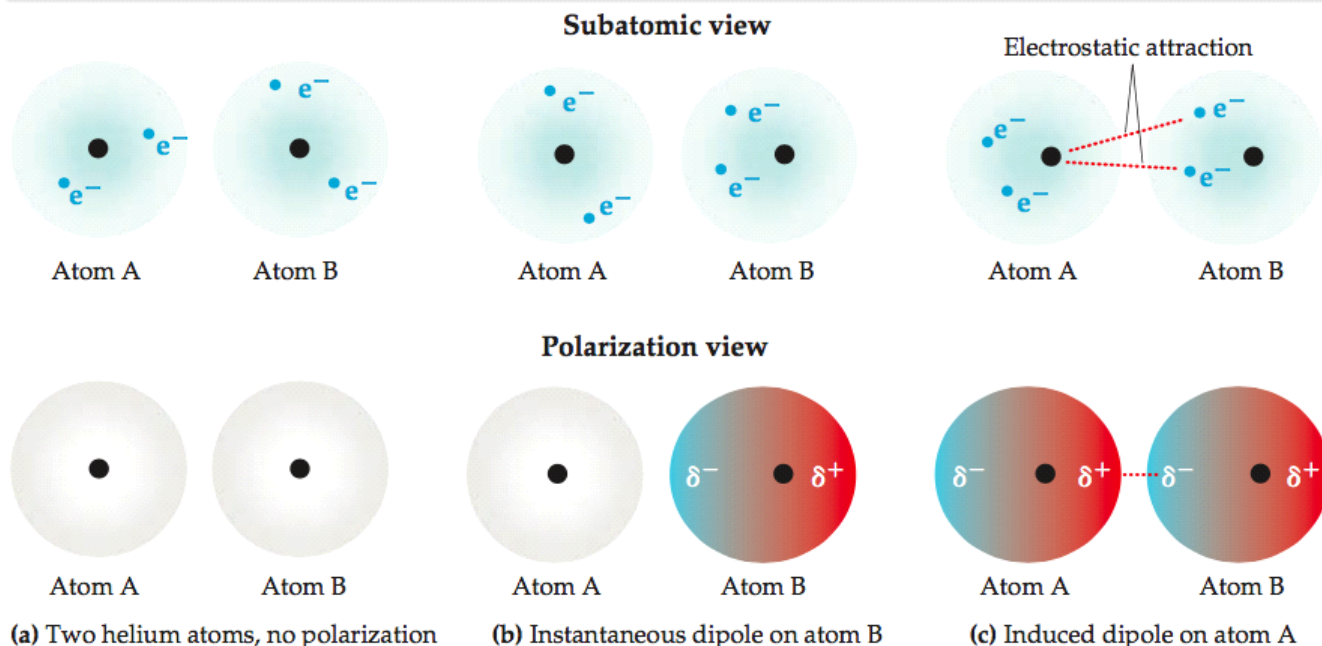
1 point is earned for comparing the solubility of ethene in water with the solubility of ethanol in water in terms of differences in polarity.

1 point is earned for describing the intermolecular forces between ethene and water as weak dipole/induced dipole forces and attributing the solubility of ethanol in water to the hydrogen bonds formed between ethanol molecules and water molecules.

The **London dispersion** force is the weakest intermolecular force. The **London dispersion** force is a temporary attractive force that results when the electrons in two adjacent atoms occupy positions that make the atoms form temporary **dipoles**. This force is sometimes called an **induced dipole-induced dipole** attraction.

London Dispersion Forces

<https://www.chem.purdue.edu/gchelp/liquids/disperse.html>



▲ **Figure 11.4 Dispersion forces.** “Snapshots” of the charge distribution for a pair of helium atoms at three instants.

Question 4 (b)

(b) Calculate the molar solubility of Ca(OH)_2 in $0.10\text{ M Ca(NO}_3)_2$.

$$K_{sp} = [\text{Ca}^{2+}] [\text{OH}^-]^2$$

$$1.3 \times 10^{-6} = (0.10 + x) (2x)^2 \approx (0.10) 4x^2 \quad \text{[assuming } x \ll 0.10\text{]}$$

$$1.3 \times 10^{-5} = 4x^2$$

$$x = 0.0018\text{ M}$$

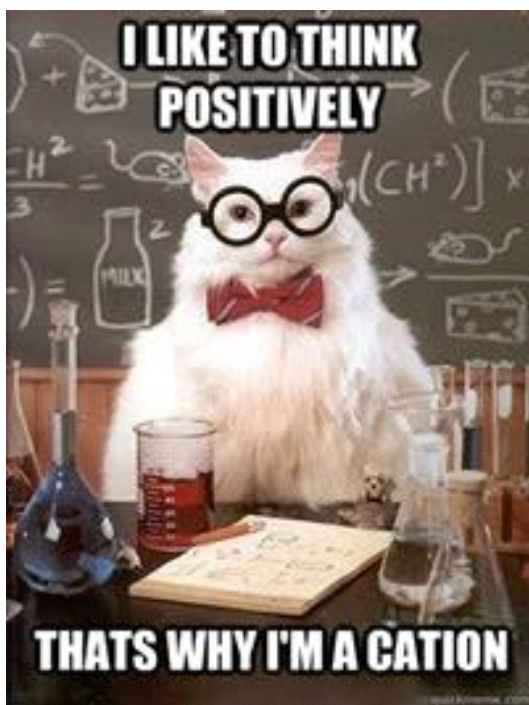
$$\text{Molar solubility of } \text{Ca(OH)}_2 = 0.0018\text{ M}$$

1 point is earned for the correct stoichiometry and setup.

1 point is earned for the final answer.

Question 6

- Anion: A Negative ION
- CATion: PAWSitive (cats have paws)



Question 7 (a)

- (a) Calculate the amount of heat needed to purify 1.00 mole of Al originally at 298 K by melting it. The melting point of Al is 933 K. The molar heat capacity of Al is 24 J/(mol·K), and the heat of fusion of Al is 10.7 kJ/mol.

To raise the temperature from 298 K to 933 K:

$$q = \frac{24 \text{ J}}{\text{mol K}} \times 1.00 \text{ mol} \times 635 \text{ K} = 15,000 \text{ J} = 15 \text{ kJ}$$

It takes 10.7 kJ to melt the Al at 933 K.

$$15 \text{ kJ} + 10.7 \text{ kJ} = 26 \text{ kJ}$$

1 point is earned for calculating the amount of heat needed to raise the temperature to 933 K.

1 point is earned for adding the heat of fusion to the previous result to get a final answer.

2016 Free Response

Wednesday, April 5, 2017 6:50 PM

Question 1 (a)

(ii) Determine the value of ΔH_{soln} for LiCl in kJ/mol_{rxn} .

$10.0 \text{ g LiCl} \times \frac{1 \text{ mol LiCl}}{42.39 \text{ g LiCl}} = 0.236 \text{ mol LiCl}$ $\frac{-9.47 \text{ kJ}}{0.236 \text{ mol LiCl}} = \boxed{-40.1} \text{ kJ/mol}_{rxn}$	1 point is earned for the number of moles of LiCl. 1 point is earned for the correct ΔH_{soln} and the correct sign.
--	---

Question 1 (c)

(c) Using principles of atomic structure, explain why the Na^+ ion is larger than the Li^+ ion.

The valence electrons in the Na^+ ion are in a higher principal energy level than the valence electrons in the Li^+ ion. Electrons in higher principal energy levels are, on average, farther from the nucleus.	1 point is earned for a correct explanation based on occupied principal energy levels.
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Question 1 (d)

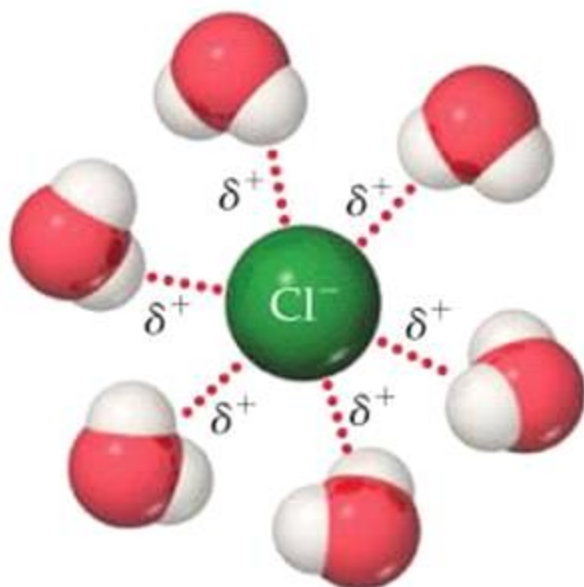
(d) Which salt, LiCl or NaCl, has the greater lattice enthalpy? Justify your answer.

LiCl. Because the Li^+ ion is smaller than the Na^+ ion, the Coulombic attractions between ions in LiCl are stronger than in NaCl. This results in a greater lattice enthalpy.	1 point is earned for the correct choice and justification.
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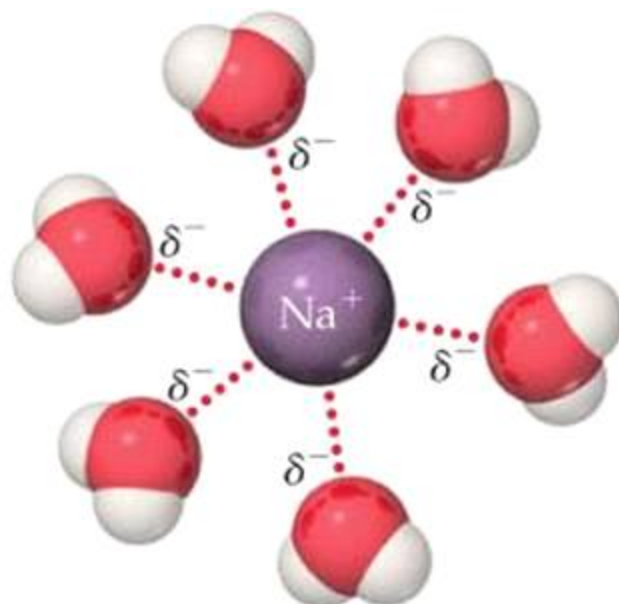
Question 1 (f)

(f) The lattice enthalpy of LiCl is positive, indicating that it takes energy to break the ions apart. in LiCl. However, the dissolution of LiCl in water is an exothermic process. Identify all particle-particle interactions that contribute significantly to the exothermic dissolution process being exothermic. For each interaction, include the particles that interact and the specific type of intermolecular force between those particles.

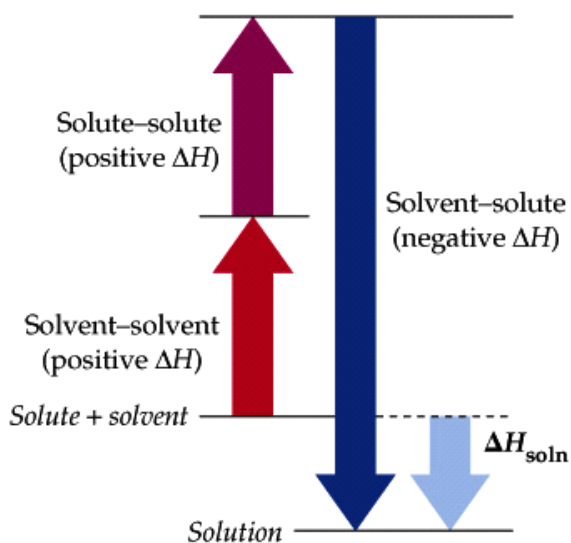
There are interactions between Li^+ ions and polar water molecules and between Cl^- ions and polar water molecules. These are ion-dipole interactions.	1 point is earned for identifying the particles that interact. 1 point is earned for correctly identifying the type of interaction.
---	--



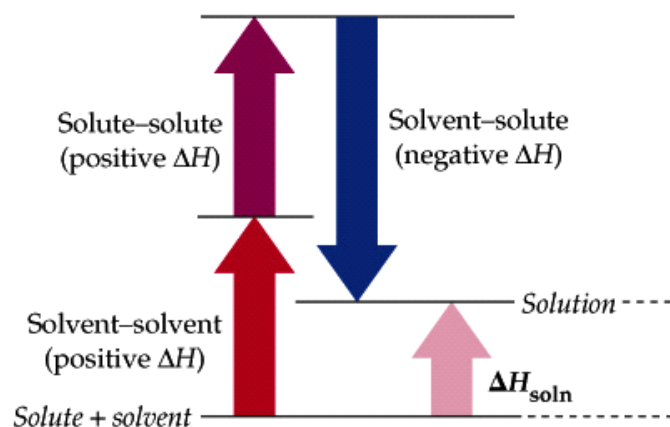
Positive ends of polar molecules are oriented toward negatively charged anion



Negative ends of polar molecules are oriented toward positively charged cation



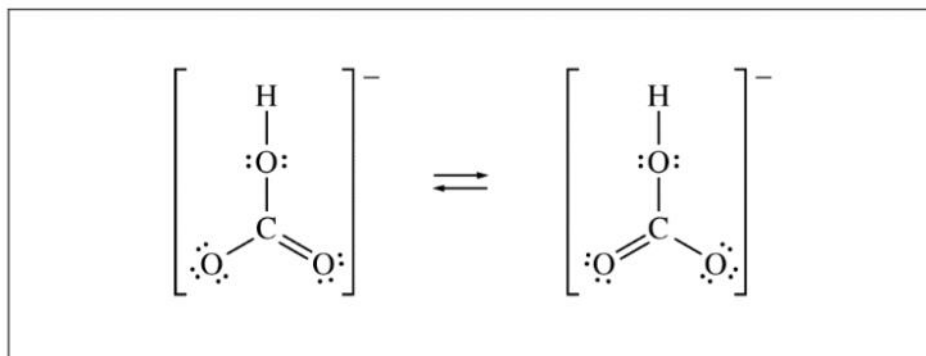
(a) Negative ΔH_{soln}



(b) Positive ΔH_{soln}

Question 2 (e)

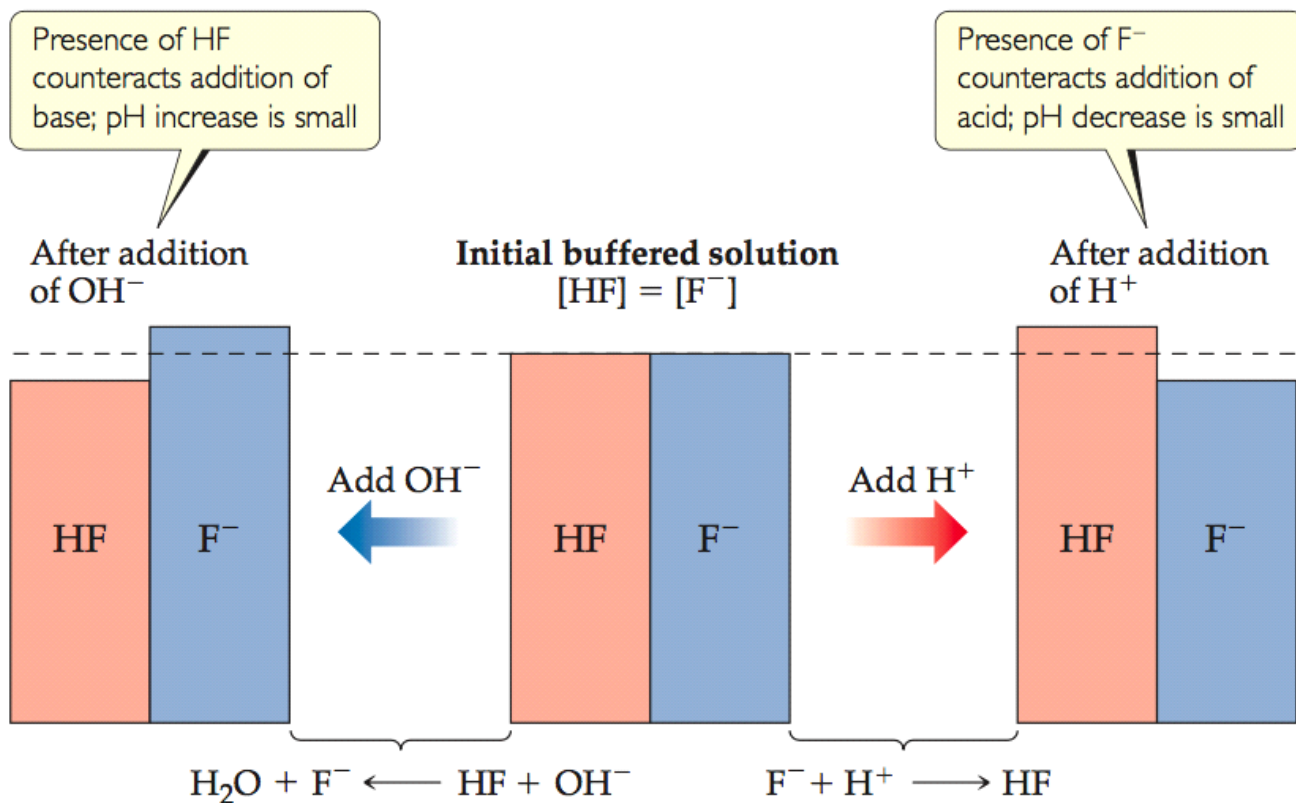
The HCO_3^- ion has three carbon-to-oxygen bonds. Two of the carbon-to-oxygen bonds have the same length and the third carbon-to-oxygen bond is longer than the other two. The hydrogen atom is bonded to one of the oxygen atoms. In the box below, draw a Lewis electron-dot diagram (or diagrams) for the HCO_3^- ion that is (are) consistent with the given information.



Question 2 (f)

- (f) A student prepares a solution containing equimolar amounts of $\text{HC}_2\text{H}_3\text{O}_2$ and $\text{NaC}_2\text{H}_3\text{O}_2$. The pH of the solution is measured to be 4.7. The student adds two drops of 3.0 M $\text{HNO}_3(\text{aq})$ and stirs the sample, observing that the pH remains at 4.7. Write a balanced, net-ionic equation for the reaction between $\text{HNO}_3(\text{aq})$ and the chemical species in the sample that is responsible for the pH remaining at 4.7.

$\text{C}_2\text{H}_3\text{O}_2^- + \text{H}_3\text{O}^+ \rightarrow \text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O}$ <p style="text-align: center;">OR</p> $\text{C}_2\text{H}_3\text{O}_2^- + \text{H}^+ \rightarrow \text{HC}_2\text{H}_3\text{O}_2$	<p>1 point is earned for a correct equation.</p>
--	--



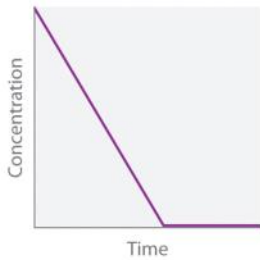

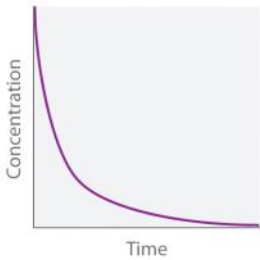
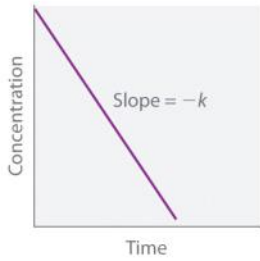


▲ **Figure 17.2 Buffer action.** The pH of an HF/F^- buffered solution changes by only a small amount in response to addition of an acid or base.

Question 3 (d)

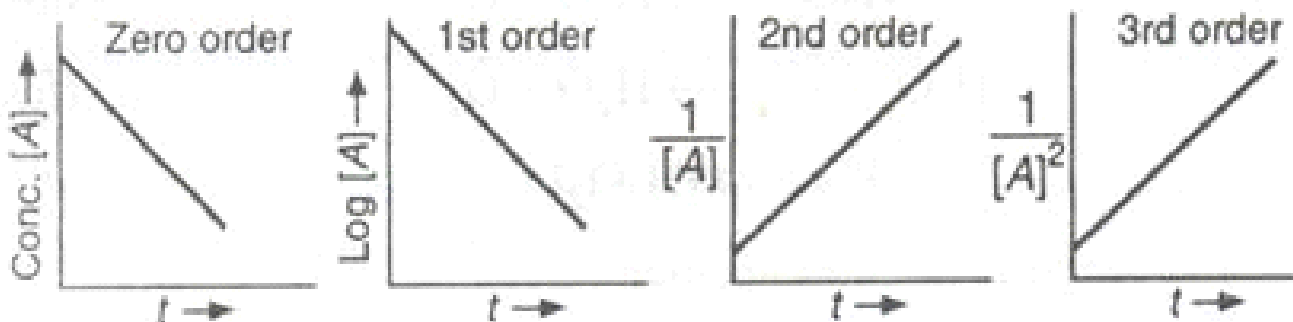
- (d) Explain why I_2 is a solid at room temperature whereas Br_2 is a liquid. Your explanation should clearly reference the types and relative strengths of the intermolecular forces present in each substance.

<p>Both Br_2 and I_2 molecules are nonpolar molecules, therefore the only possible intermolecular forces are London dispersion forces.</p> <p>The London dispersion forces are stronger in I_2 because it is larger in size with <u>more electrons and/or a more polarizable electron cloud</u>. The stronger London dispersion forces in I_2 result in a higher melting point, which makes I_2 a solid at room temperature.</p>	<p>1 point is earned for identifying the forces in each substance as London dispersion forces.</p> <p>1 point is earned for explaining why the forces are stronger in I_2 than in Br_2.</p>
--	---

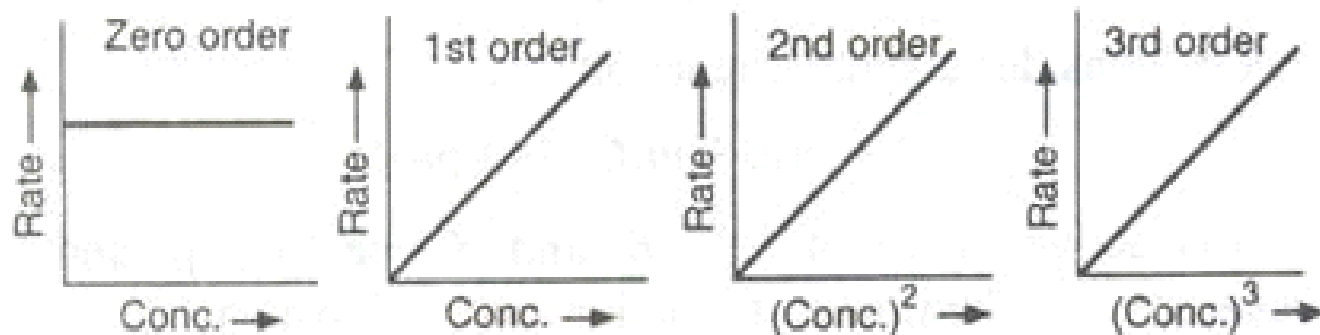
Question 5 (b)

	Zeroth Order	First Order	Second Order																								
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$																								
Concentration vs. time																											
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$																								
Straight-line plot to determine rate constant																											
Relative rate vs. concentration	<table><thead><tr><th>[A], M</th><th>Rate, M/s</th></tr></thead><tbody><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>1</td></tr><tr><td>3</td><td>1</td></tr></tbody></table>	[A], M	Rate, M/s	1	1	2	1	3	1	<table><thead><tr><th>[A], M</th><th>Rate, M/s</th></tr></thead><tbody><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>2</td></tr><tr><td>3</td><td>3</td></tr></tbody></table>	[A], M	Rate, M/s	1	1	2	2	3	3	<table><thead><tr><th>[A], M</th><th>Rate, M/s</th></tr></thead><tbody><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>4</td></tr><tr><td>3</td><td>9</td></tr></tbody></table>	[A], M	Rate, M/s	1	1	2	4	3	9
[A], M	Rate, M/s																										
1	1																										
2	1																										
3	1																										
[A], M	Rate, M/s																										
1	1																										
2	2																										
3	3																										
[A], M	Rate, M/s																										
1	1																										
2	4																										
3	9																										
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$																								
Units of k, rate constant	M/s	1/s	M ⁻¹ ·s ⁻¹																								

Order	Rate Law	Concentration - Time Equation	Half Life	Graphical Plot
0	Rate = k_0	$[A]_0 - [A] = k_0 t$	$\frac{[A]_0}{2k_0}$	$[A]$ vs t
1	Rate = $k_1 [A]$	$\log \frac{[A]_0}{[A]} = \frac{k t}{2.303}$	$\frac{0.693}{k}$	$\log A$ vs t
2	Rate = $k_2 [A]^2$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$	$\frac{1}{(k_2 [A]_0)}$	$\frac{1}{[A]}$ vs t



(b) Plots from integrated rate equations:



Question 6 (a)

- (a) Considering the value of K for the reaction, determine the concentration of $\text{Ba}(\text{EDTA})^{2-}(\text{aq})$ in the 100.0 mL of solution. Justify your answer.

Based on the K value, the reaction goes essentially to completion. $\text{Ba}^{2+}(\text{aq})$ is the limiting reactant.

The concentration of Ba^{2+} when the solutions are first mixed but before any reaction takes place is $0.20 \text{ M}/2 = 0.10 \text{ M}$.

Thus the equilibrium concentration of $\text{Ba}(\text{EDTA})^{2-}(\text{aq})$ is 0.10 M .

1 point is earned for indicating that the equilibrium concentration of $\text{Ba}(\text{EDTA})^{2-}(\text{aq})$ is the same as the original concentration of Ba^{2+} when the solutions are mixed.

1 point is earned for the concentration with appropriate calculations.

Question 7 (a)

- Since your buret is graduated to 0.1 mL, you will read your buret to 0.01 mL. The second decimal place is an estimate, but should be recorded.

Practice Test Multiple Choice

2017年2月8日 星期三 下午 12:05

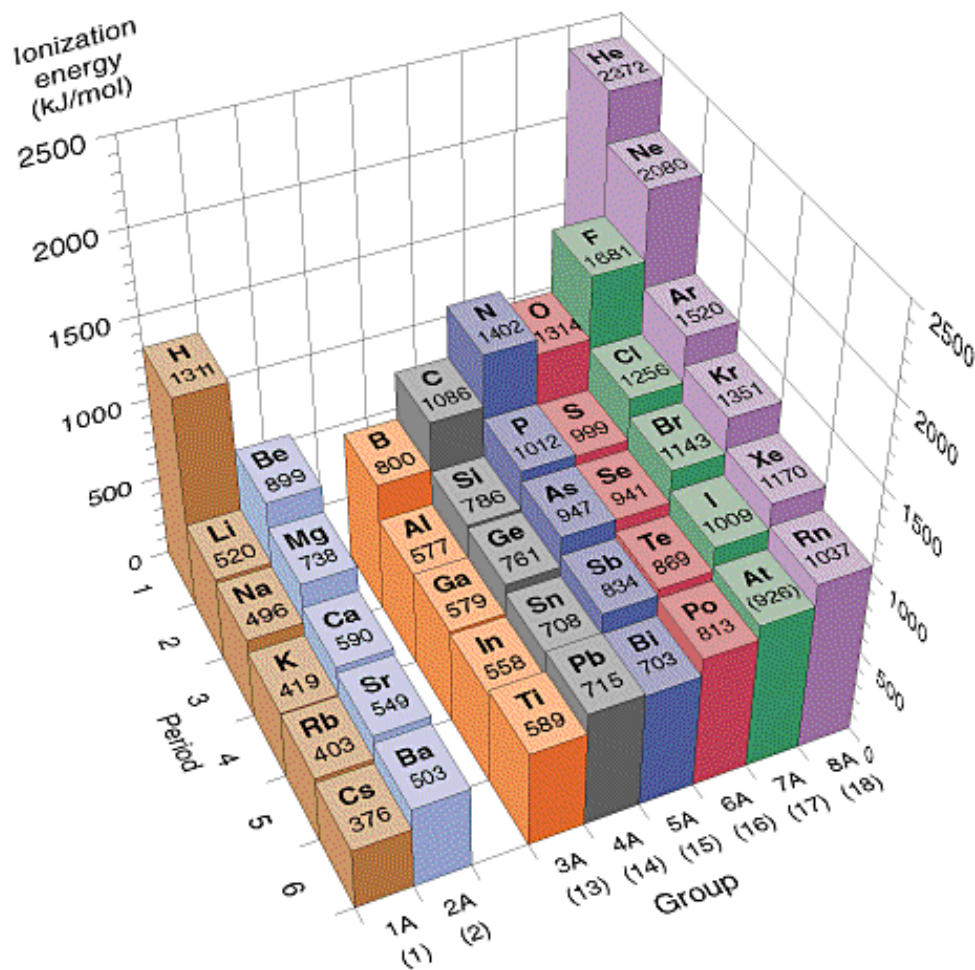
Question 4

- Potassium Chromate is a **yellowish**, crystalline compound.



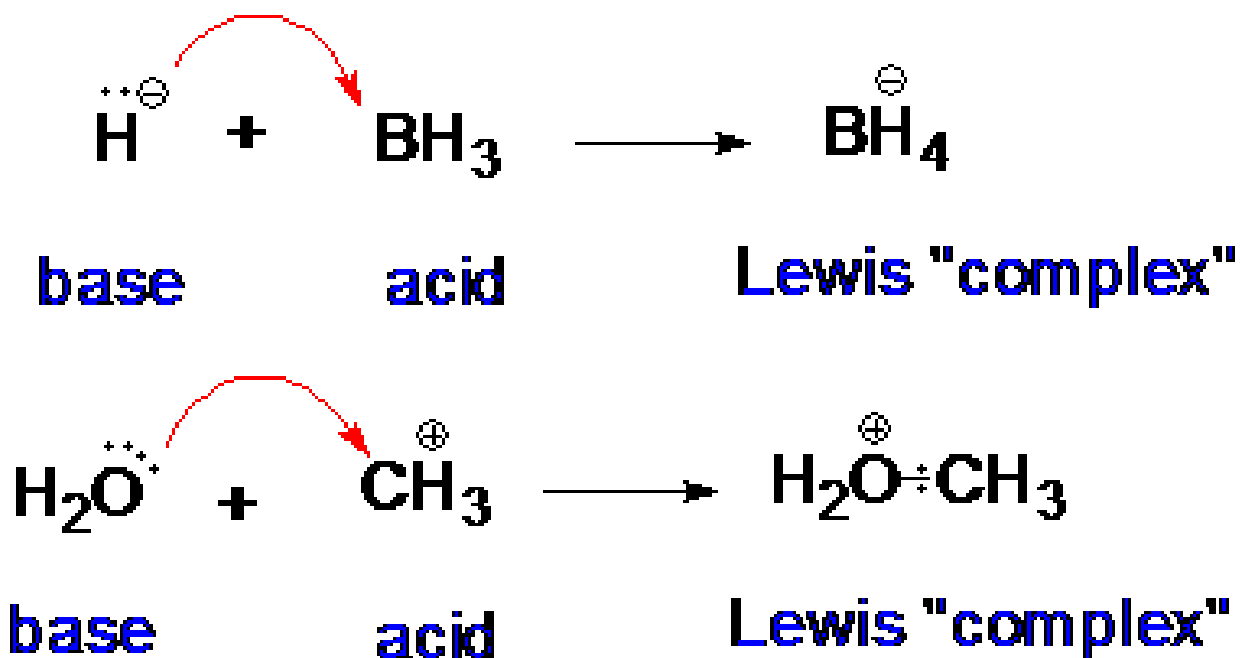
Question 10

- First Ionization Energy: He > Ne > Ar > Kr > Xe



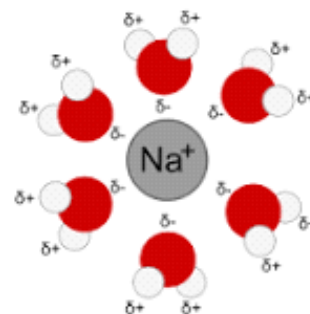
Question 15

- A typical Lewis acid-base reaction:



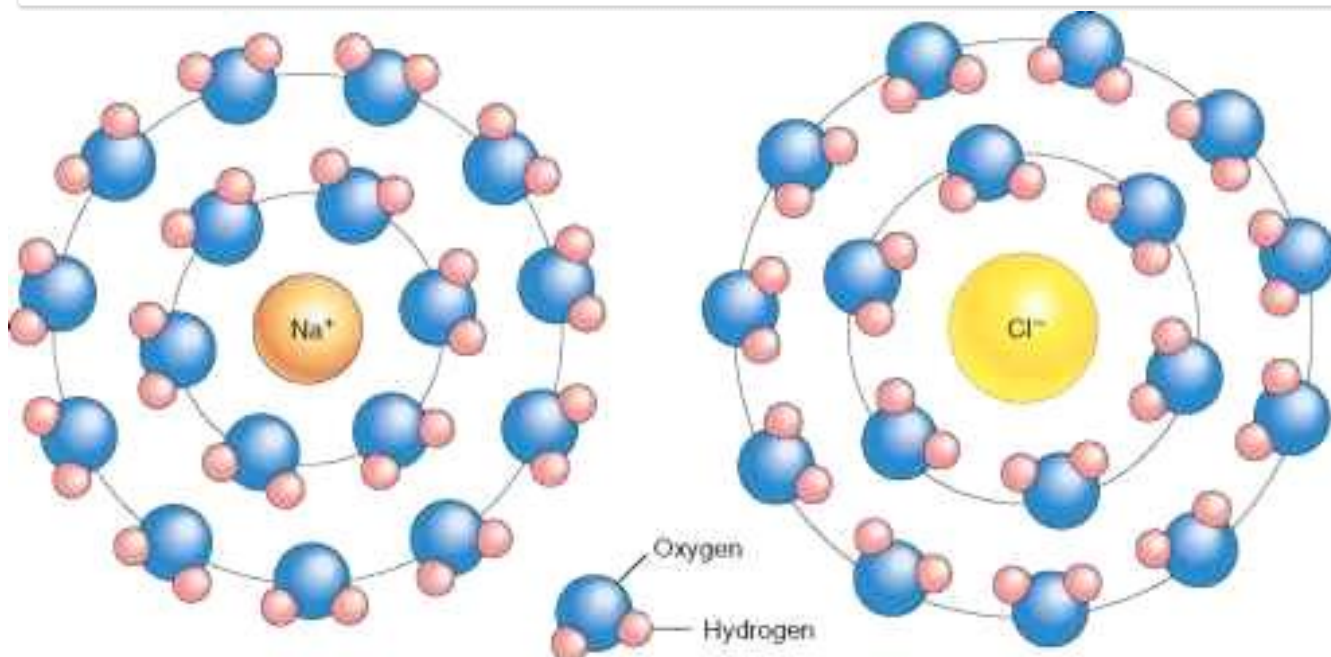
Question 23

A **solvation shell** is the solvent interface of any chemical compound or biomolecule that constitutes the solute. When the solvent is water it is often referred to as a **hydration shell** or **hydration sphere**. A classic example is when water molecules arrange around a metal ion.



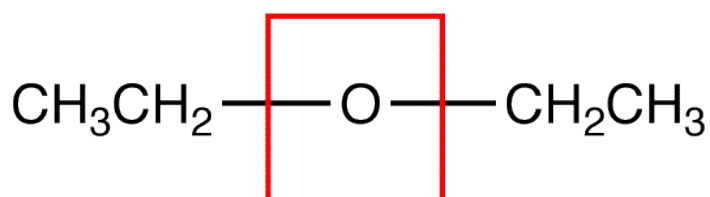
Solvation shell - Wikipedia

https://en.wikipedia.org/wiki/Solvation_shell



- For the process of solid calcium chloride **dissolving in water**, the **entropy** change is **negative** since **water molecules** in the hydration shells of Ca^{2+} and Cl^- ions are **more ordered** than they are in the pure water

Question 28

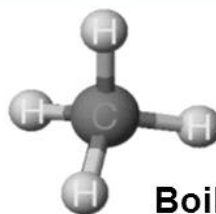
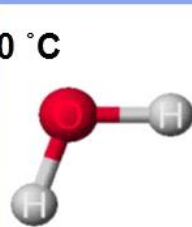


ether group

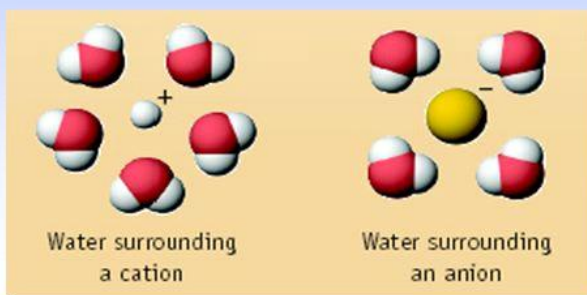
Question 30

Molecular Polarity

Boiling point = $100\text{ }^{\circ}\text{C}$



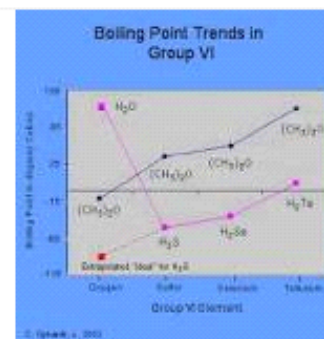
Boiling point = $-161\text{ }^{\circ}\text{C}$



Why do ionic compounds dissolve in water?

Why do water and methane differ so much in their boiling points?

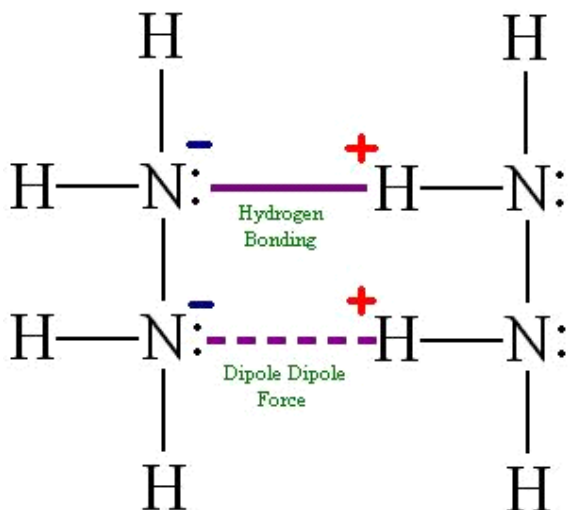
Polarity and Boiling Point: The **polarity** of the molecules determines the forces of attraction between the molecules in the liquid state. Polar molecules are attracted by the opposite charge effect (the positive end of one molecule is attracted to the negative end of another molecule).



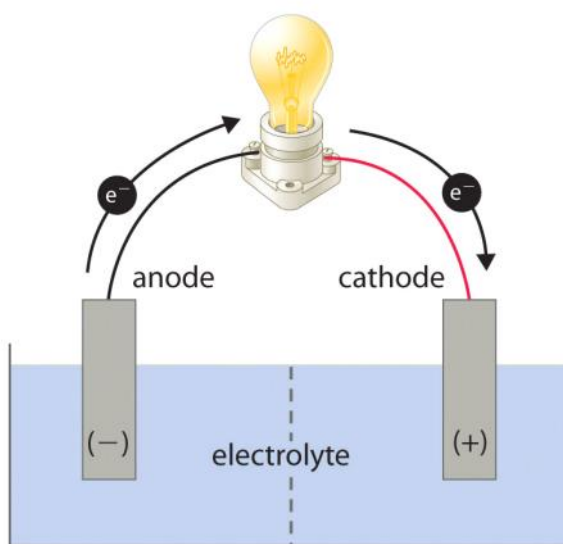
Hydrogen Bonds and Boiling Point - Chemistry@Elmhurst
chemistry.elmhurst.edu/vchembook/163boilingpt.html

Question 34

- N_2H_4 exhibits **significant hydrogen bonding** in the liquid state.



Question 37



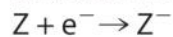
GALVANIC CELL

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

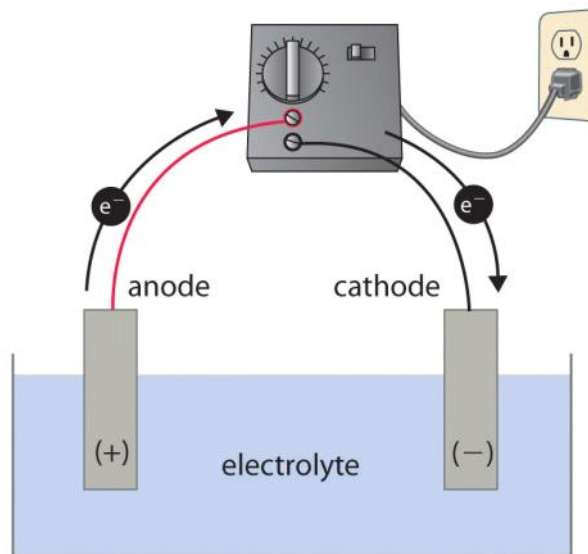
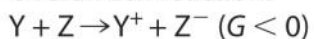
Oxidation half-reaction:



Reduction half-reaction:



Overall cell reaction:



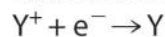
ELECTROLYTIC CELL

Electrical energy is used to drive nonspontaneous redox reaction.

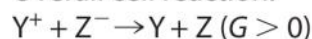
Oxidation half-reaction:



Reduction half-reaction:

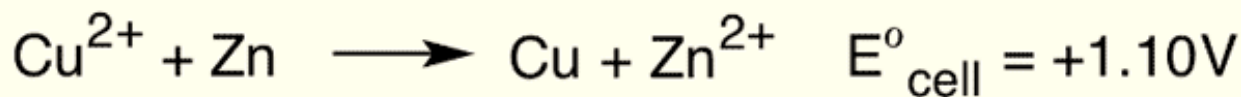
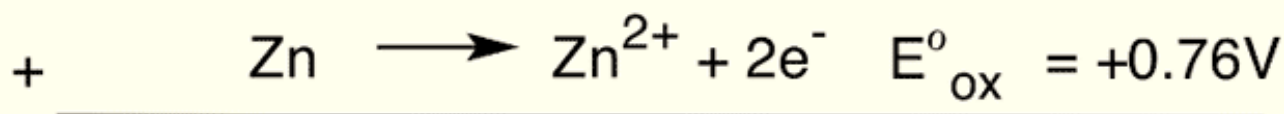
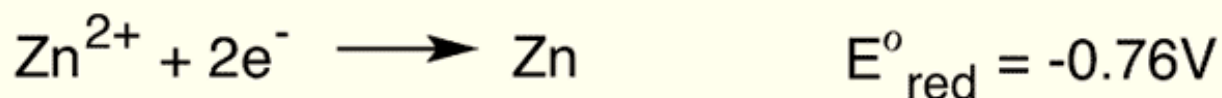
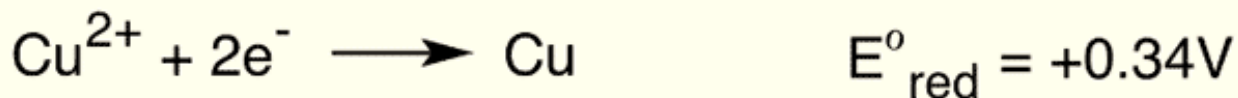


Overall cell reaction:



Question 38

- Calculate standard cell potential for the galvanic cell:



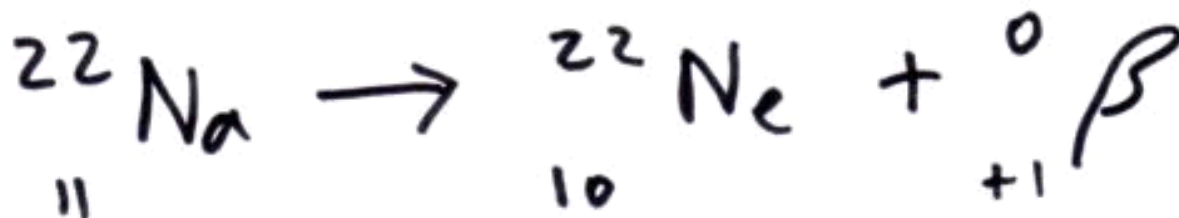
$$E = E^{\circ} - \frac{RT}{nF} \ln Q$$

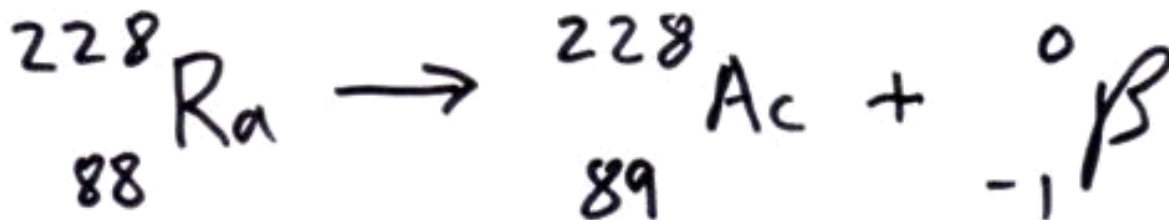
$$= 1.10\text{V} - \frac{(8.31 \text{ J/mol K})(298\text{K})}{(2 \text{ mol})(96500 \text{ C/mol})} \ln \frac{(1.75)}{(0.100)}$$

$$= 1.06\text{V}$$

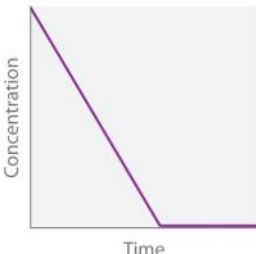
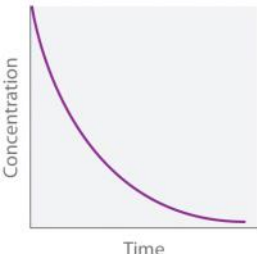
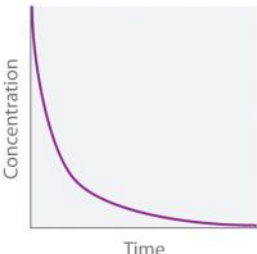
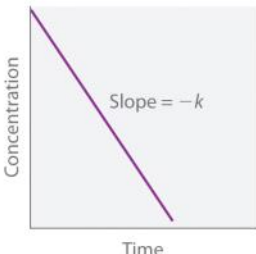

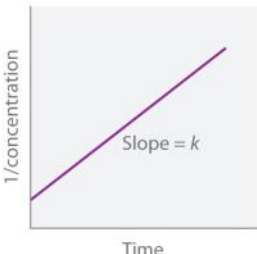
Question 40

- Beta plus decay vs Beta minus decay

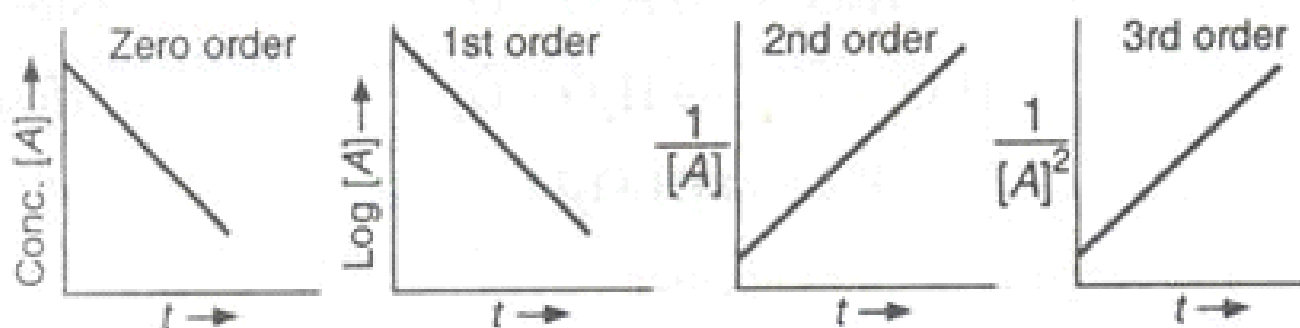




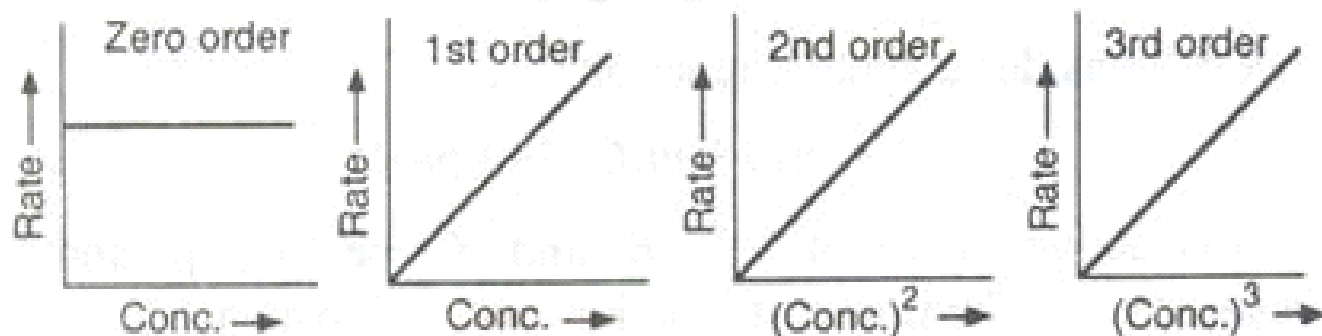
Question 47

	Zeroth Order	First Order	Second Order																								
Differential rate law	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]$	$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^2$																								
Concentration vs. time																											
Integrated rate law	$[A] = [A]_0 - kt$	$[A] = [A]_0 e^{-kt}$ or $\ln[A] = \ln[A]_0 - kt$	$\frac{1}{[A]} = \frac{1}{[A]_0} + kt$																								
Straight-line plot to determine rate constant																											
Relative rate vs. concentration	<table><tr><th>[A], M</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>1</td></tr><tr><td>3</td><td>1</td></tr></table>	[A], M	Rate, M/s	1	1	2	1	3	1	<table><tr><th>[A], M</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>2</td></tr><tr><td>3</td><td>3</td></tr></table>	[A], M	Rate, M/s	1	1	2	2	3	3	<table><tr><th>[A], M</th><th>Rate, M/s</th></tr><tr><td>1</td><td>1</td></tr><tr><td>2</td><td>4</td></tr><tr><td>3</td><td>9</td></tr></table>	[A], M	Rate, M/s	1	1	2	4	3	9
[A], M	Rate, M/s																										
1	1																										
2	1																										
3	1																										
[A], M	Rate, M/s																										
1	1																										
2	2																										
3	3																										
[A], M	Rate, M/s																										
1	1																										
2	4																										
3	9																										
Half-life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{0.693}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$																								
Units of k, rate constant	M/s	1/s	M ⁻¹ ·s ⁻¹																								

Order	Rate Law	Concentration - Time Equation	Half Life	Graphical Plot
0	Rate = k_0	$[A]_0 - [A] = k_0 t$	$\frac{[A]_0}{2k_0}$	$[A]$ vs t
1	Rate = $k_1 [A]$	$\log \frac{[A]_0}{[A]} = \frac{k t}{2.303}$	$\frac{0.693}{k}$	$\log A$ vs t
2	Rate = $k_2 [A]^2$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$	$\frac{1}{(k_2 [A]_0)}$	$\frac{1}{[A]}$ vs t

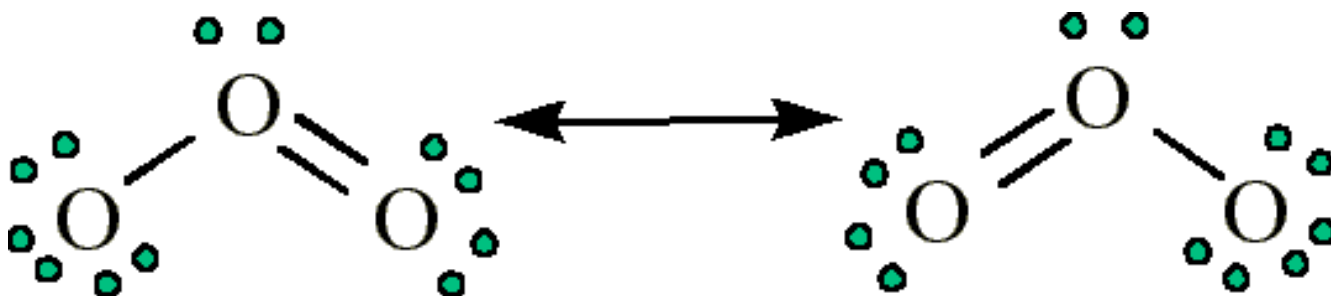


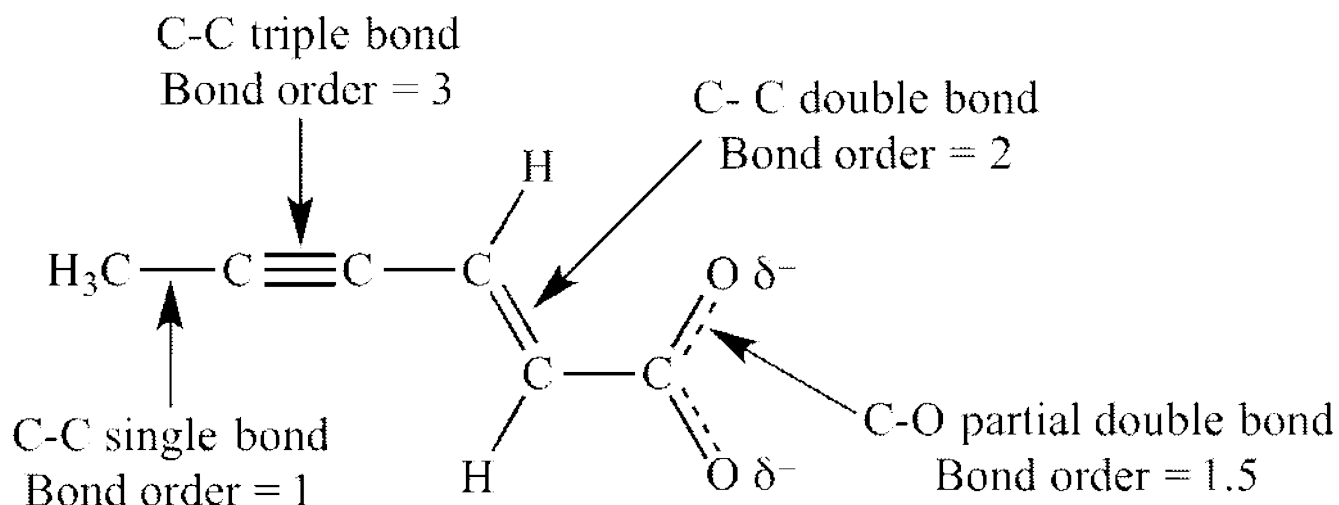
(b) Plots from integrated rate equations:



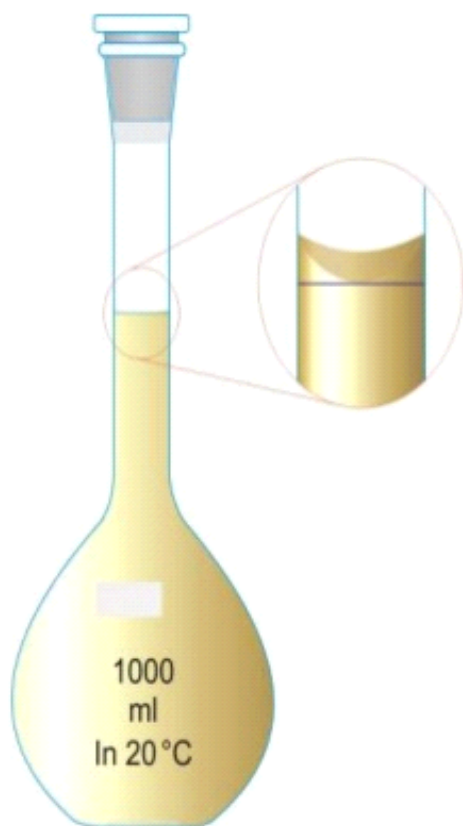
Question 51

- O₃** contains bonds that have a **bond order** of 1.5

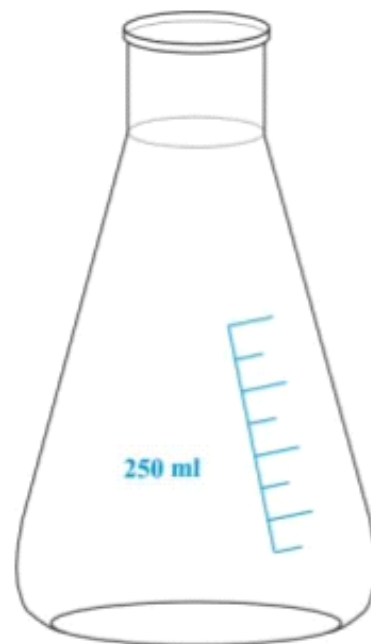




Question 67



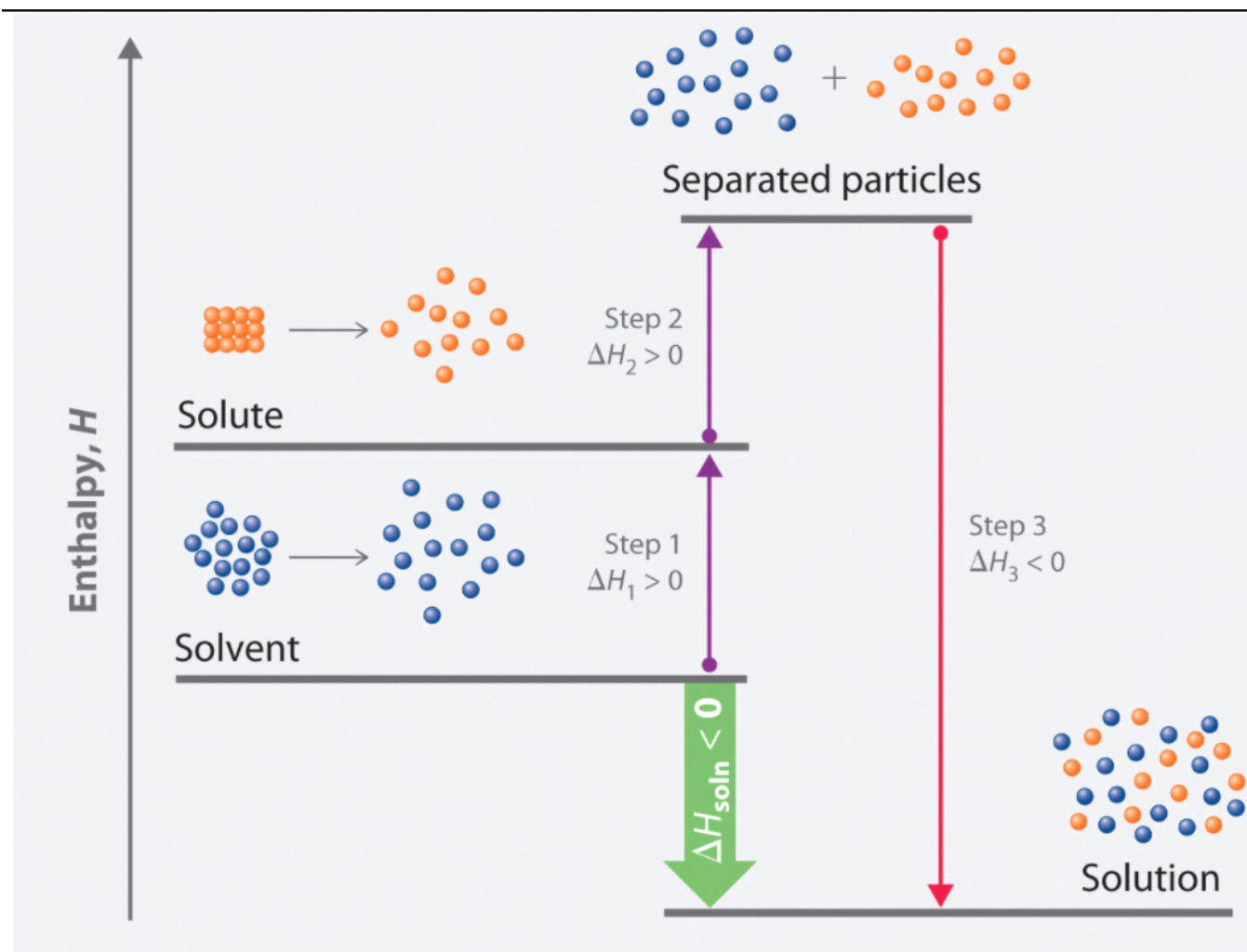
Volumetric Flask



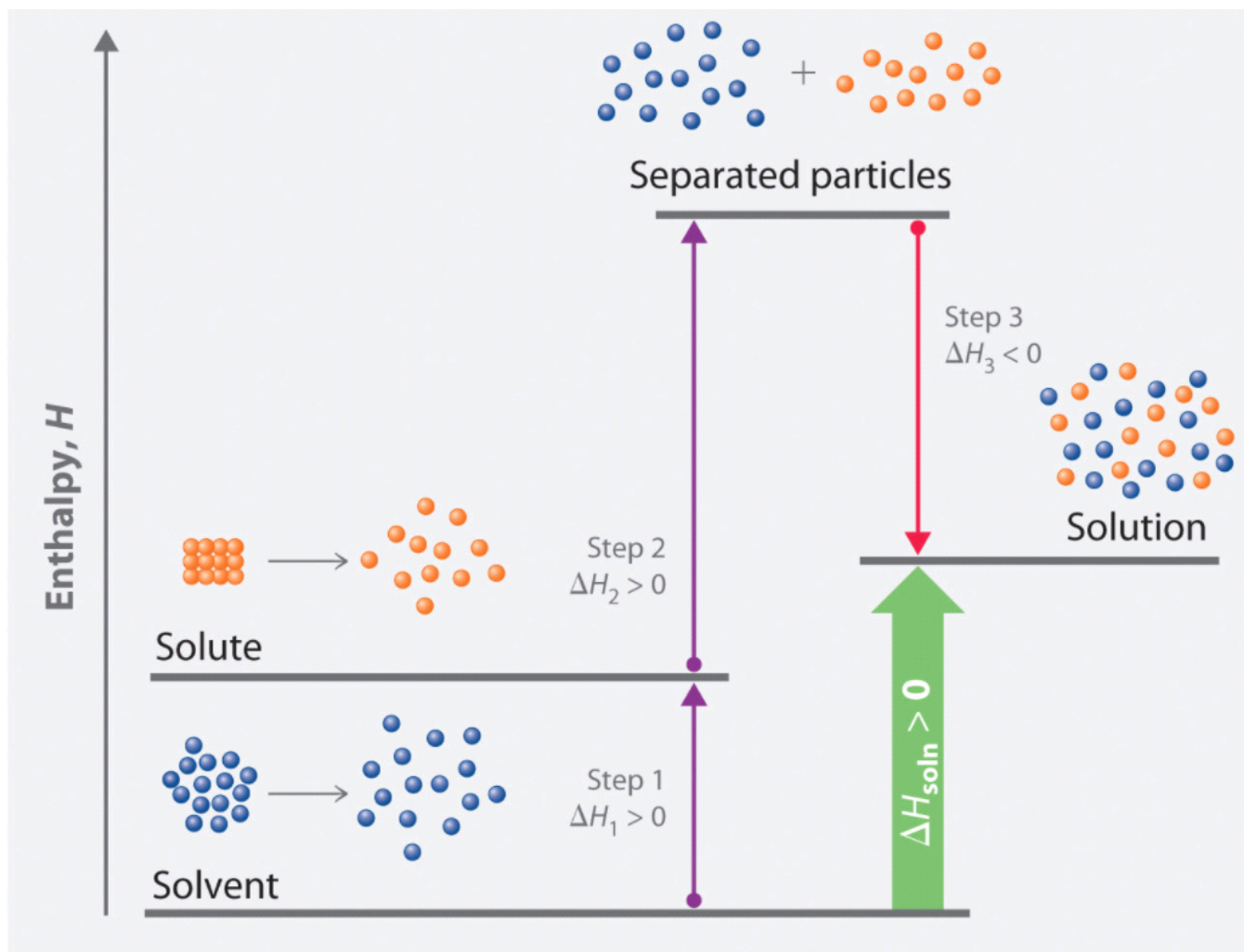
Conical (Erlenmeyer) flasks

Question 71

- **Endothermic:** Separation of solute and solvent
- **Exothermic:** Intermolecular attractions **form** between solute and solvent



(a) Exothermic solution formation



(b) Endothermic solution formation

Princeton 1 Multiple Choice

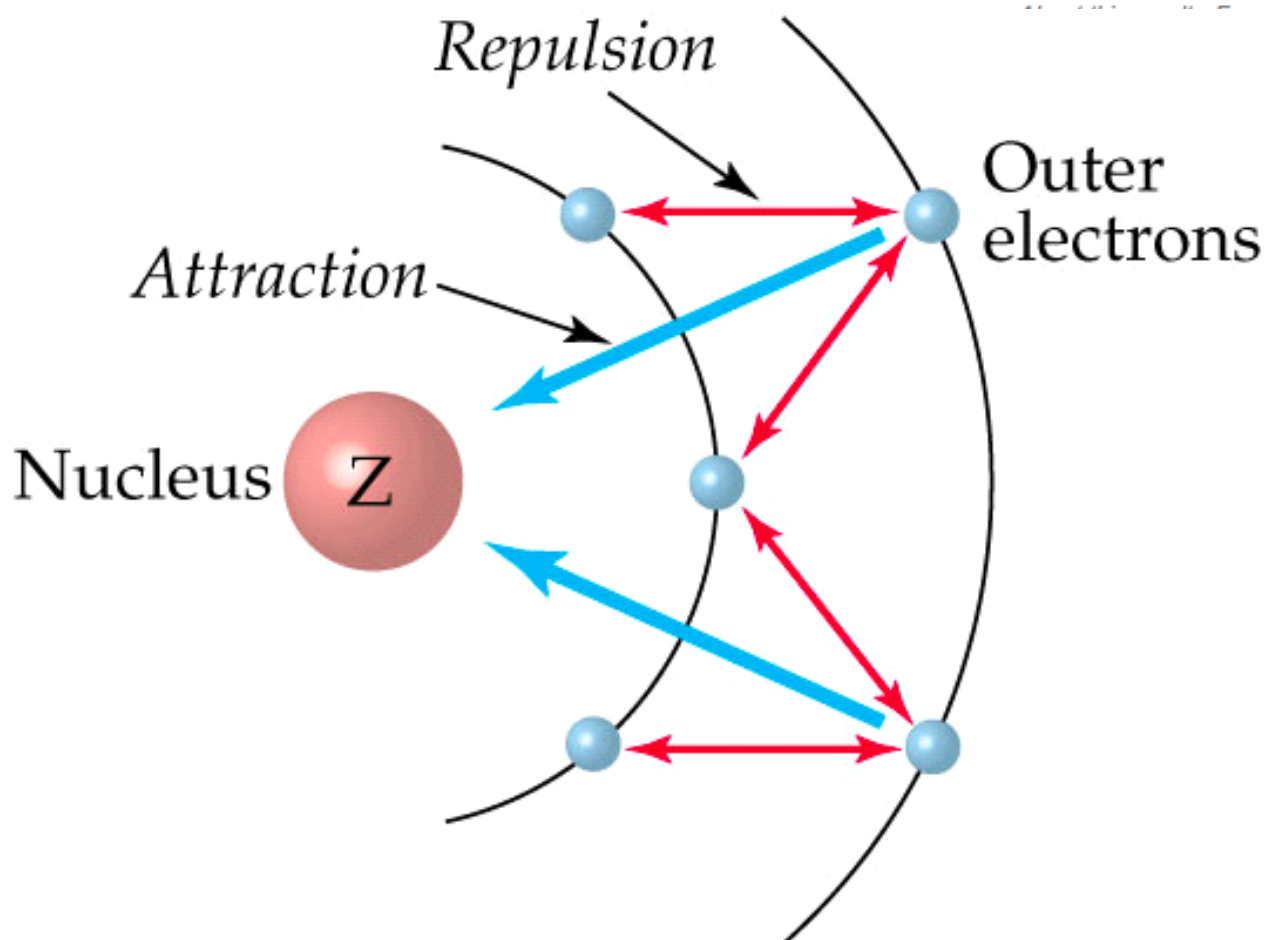
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Question 3

The **shielding effect** describes the attraction between an **electron** and the nucleus in any atom with more than one **electron shell**. **Shielding effect** can be defined as a reduction in the effective nuclear charge on the **electron** cloud, due to a difference in the attraction forces of the **electrons** on the nucleus.

Shielding effect - Wikipedia

https://en.wikipedia.org/wiki/Shielding_effect

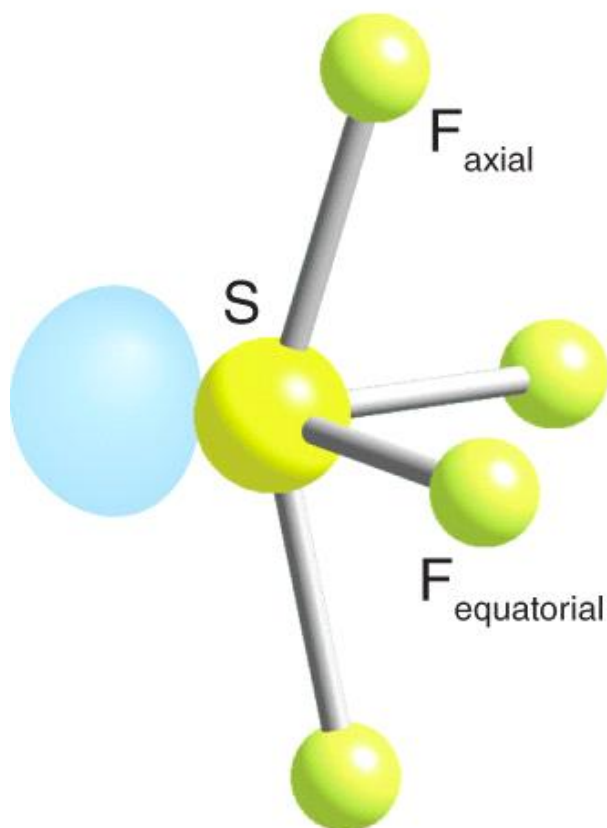


Question 9

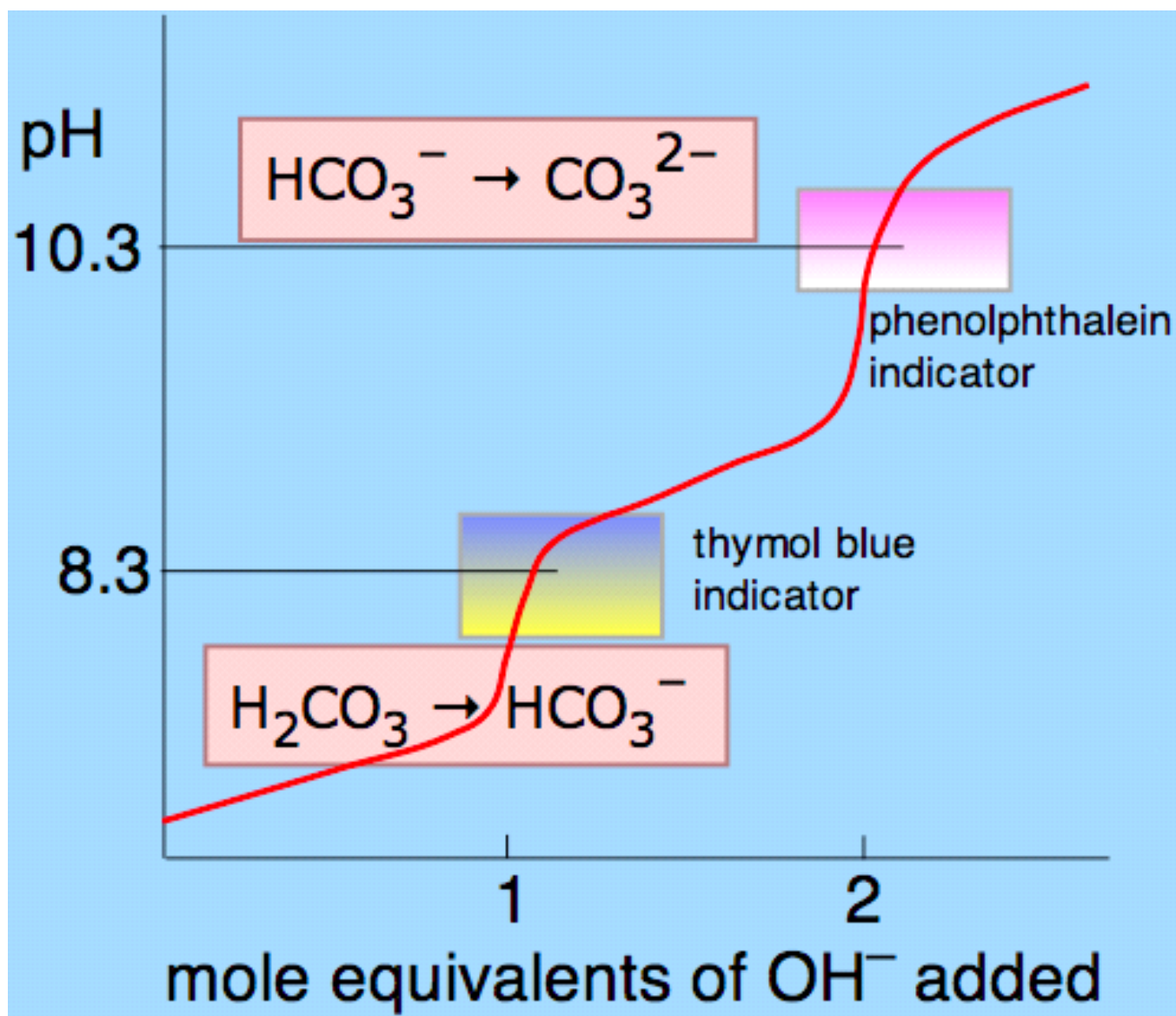
- In an **electrochemical reaction**, as the reaction progress, the **voltage** of the cell will **decrease** because with a lower concentration, the number of electrons that are being transferred will decrease

Question 12

- **SF₄** has an **asymmetrical** molecular structure

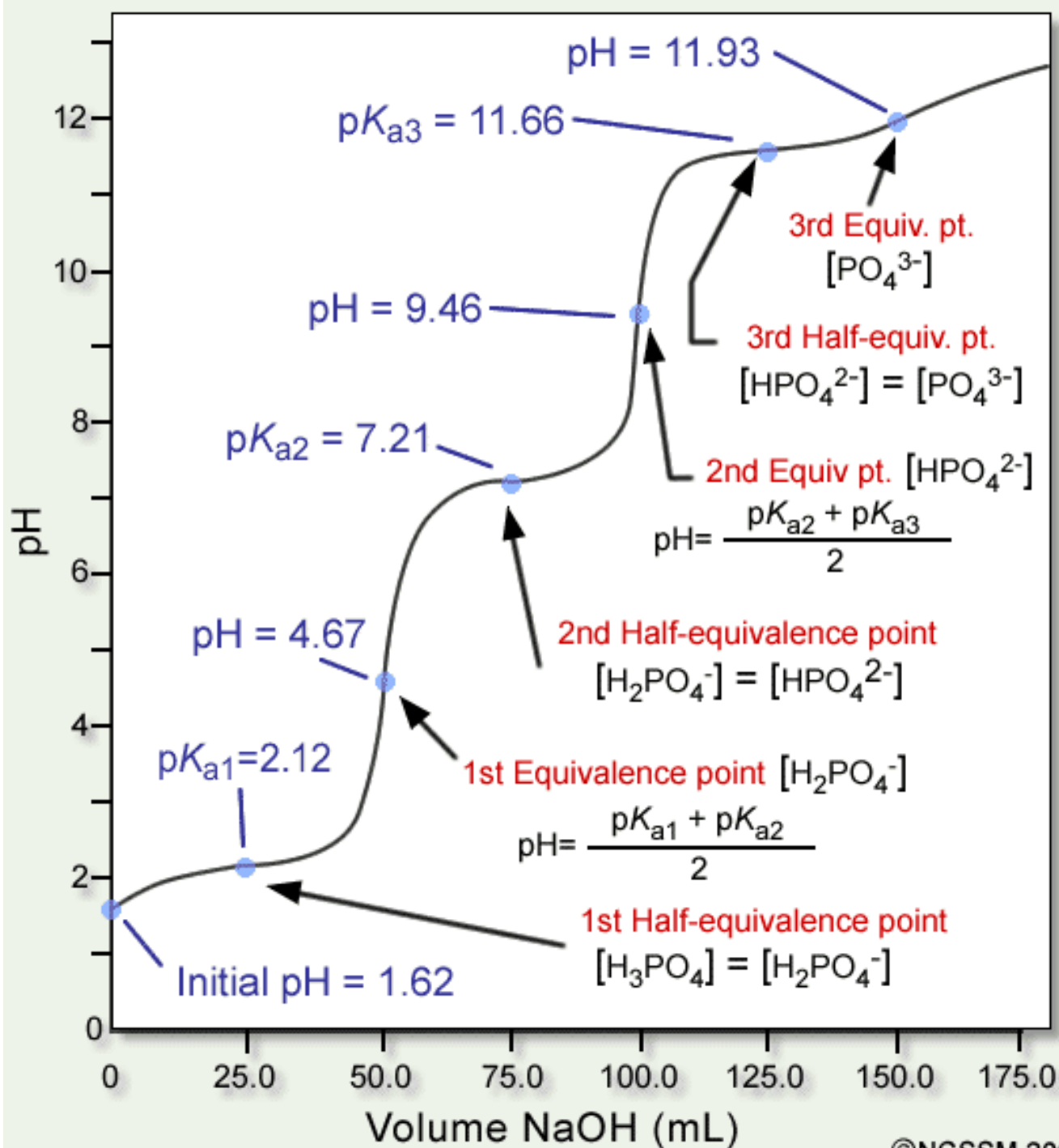


Question 16



Question 17

Titration of 50.0mL of 0.100M H_3PO_4
with 0.100M NaOH



Henderson-Hasselbalch Equation

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

$\frac{[\text{A}^-]}{[\text{HA}]}$ — Conjugate Base
 — Weak Acid

- At the **half-equivalence point**, the last part of the Henderson-Hasselbalch equation cancels out, leaving **pH=pKa**

Question 20

$$\Delta G^\circ = -RT \ln(K_{eq})$$

Question 21

- The weaker the O-H bond is in an oxoacid, the stronger the acid will be as the H^+ ions are more likely to dissociate. The O-F bond in HOF is stronger than the O-Cl bond in HOCl because fluorine is smaller (and thus more electronegative) than chlorine. If the O-F bond is stronger, the O-H bond is correspondingly weaker, making HOF the stronger acid.

Question 23

- **Buffer = a weak acid/base + its salt**

Question 27

- With the same amount of limiting reactant, adding more excessive reactant will not change the value for H , but the change in temperature will decrease for the increase in overall mass

Question 38

- At **low temperatures** or **high pressures**, real gases **deviate** significantly from ideal gas behavior.

Question 49

- The **overall** rate law is always equal to the **rate law** for the **slowest** elementary step, which can be determined using the **coefficients** of the **reactants**. In this case, $\text{rate} = k[\text{NO}_2][\text{F}_2]$. To get the overall order, we **add** the **exponents** in the rate law. $1 + 1 = 2$

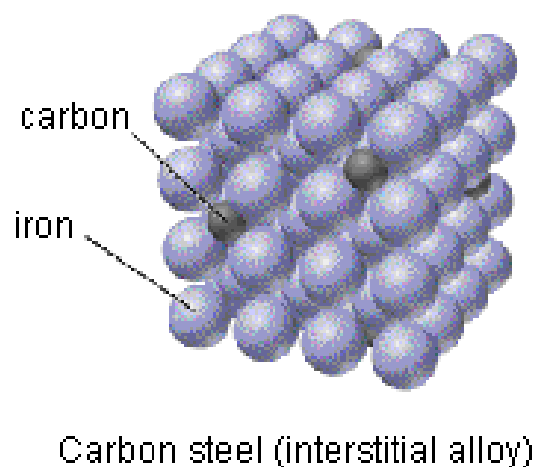
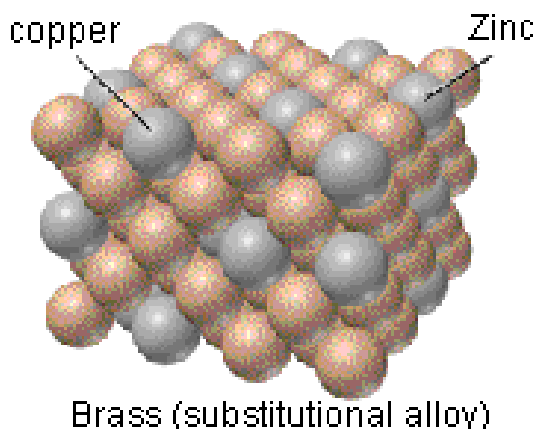
Question 53

- Lower vapor pressure = weaker IMFs
- IMFs:
 - polar > nonpolar
 - with hydrogen bonding > without hydrogen bonding

Question 55

- If both nonpolar, **more electron** = **more polarizable** = stronger IMFs = higher boiling point

Question 60



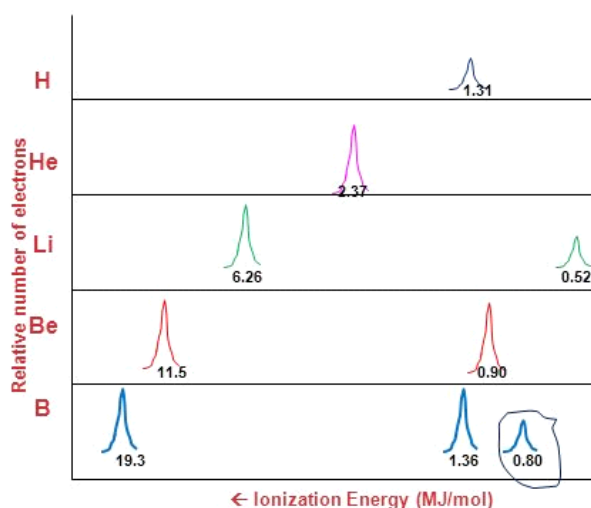
- Substitutional** alloys have **similar, reduced malleability** and **ductility** to interstitial alloys and have densities that typically lay between the densities of the component metals

Question 11

- The **further away** an electron is from the nucleus, the **less binding energy** that the incoming photons need to overcome, and as a result, the **more kinetic energy** the electron will have after it is ejected.

Question 20

Photoelectron Spectroscopy PES



- The shell model does not separate the 8 electrons in $n = 2$. But The PES for boron does not support that.
- PES data tells us that the model must be revised, as the $n = 2$ shell must contain 2 subshells with different IE.
- Each peak corresponds to a subshell or sublevel.**

H: 1 electron in $n = 1$

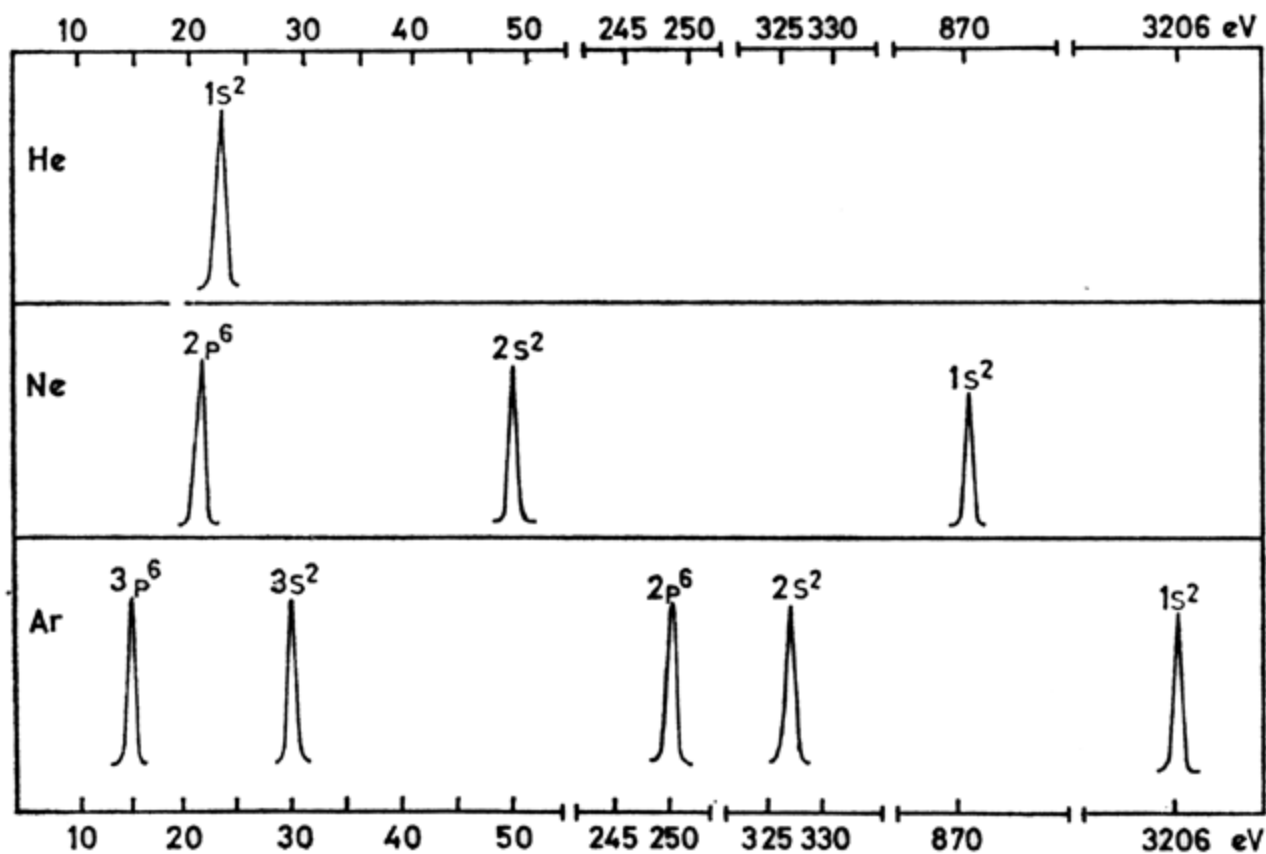
He: 2 electrons in $n = 1$

Li: 2 electrons in $n = 1$ and 1 electrons in $n = 2$

Be: 2 electrons in $n = 1$ and 2 electrons in $n = 2$

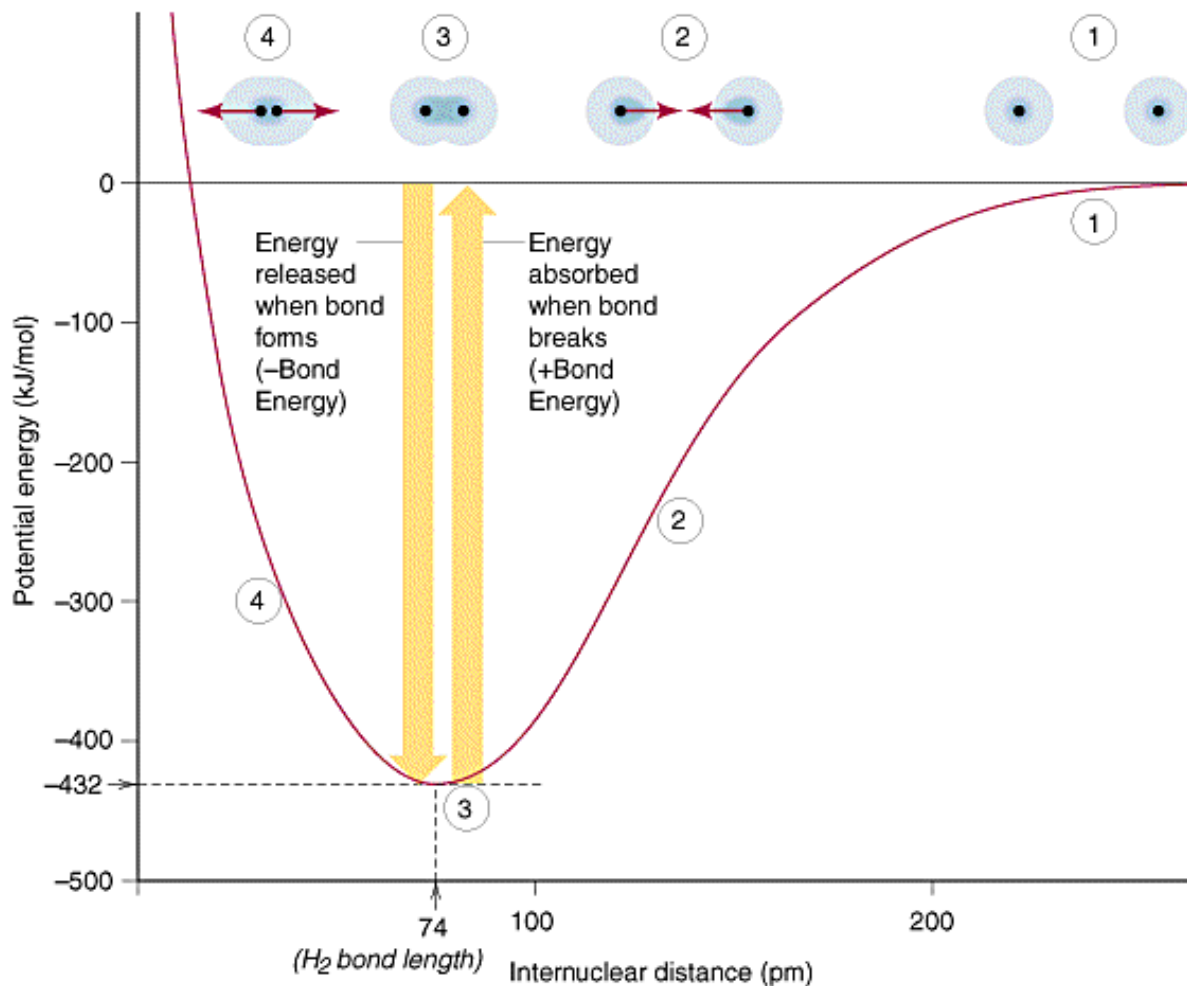
B: 2 electrons in $n = 1$, 2 electrons in $n = 2$, 2s and 1 electron in 2p





Question 21

The **bond length** always corresponds to the point where the **potential bond energy** (a balance of the attraction and repulsion forces between the two atoms) is at its **minimum** value.

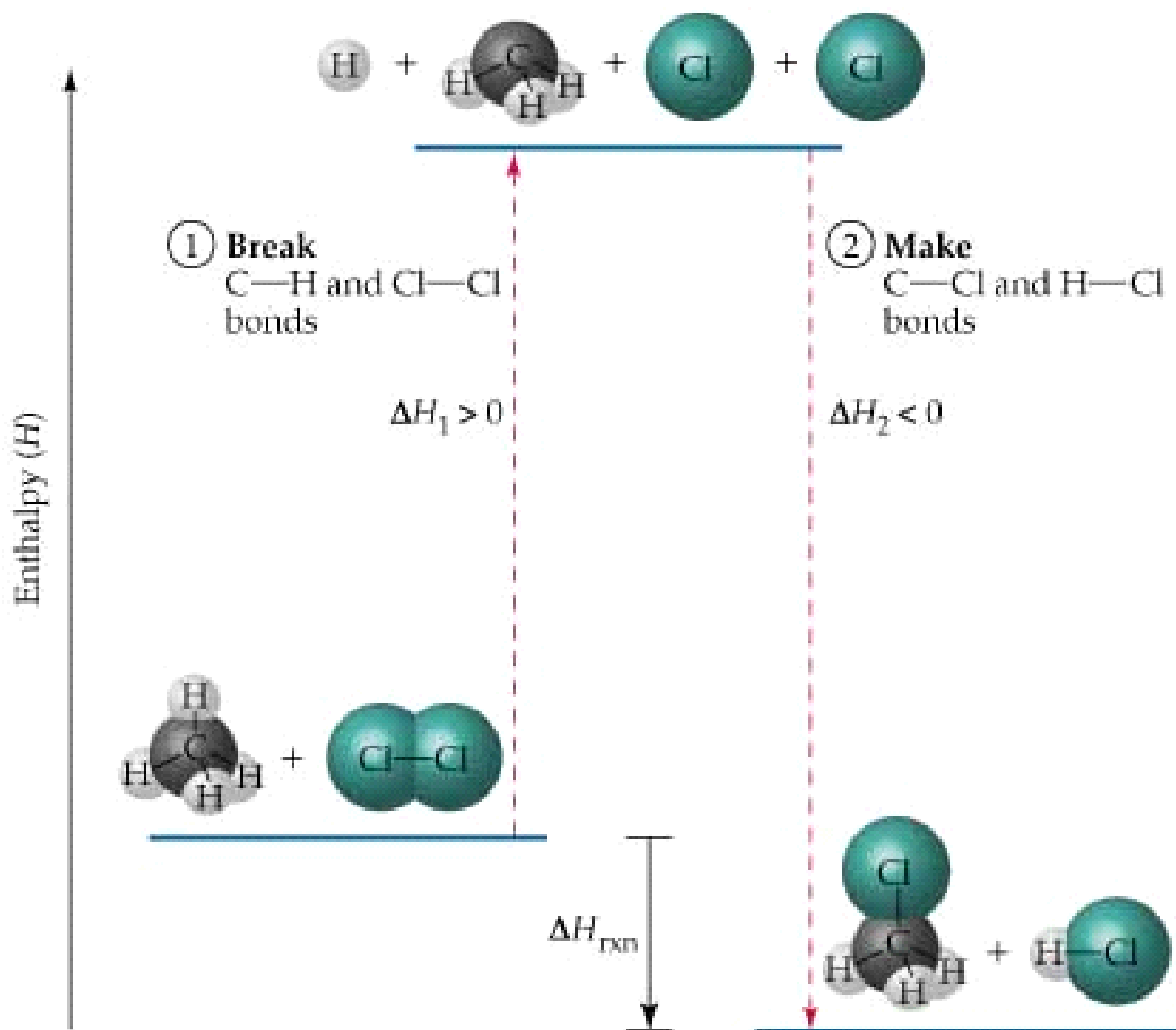


Question 23

- **Weak acids resist changes in pH** more effectively than strong acids because so many molecules of weak acid are **undissociated** in solution. The base must cause those molecules to dissociate before affecting the pH significantly.

Question 25

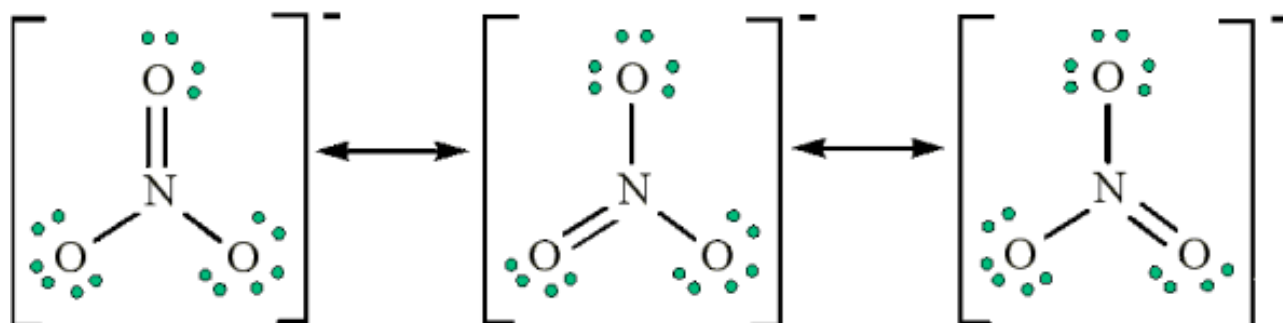
- When calculating enthalpy, the **total energy** is always the **bonds broken** (reactants) **minus** the **bonds formed** (products). The more positive this value is, the more energy there is in the reactants compared to the products.

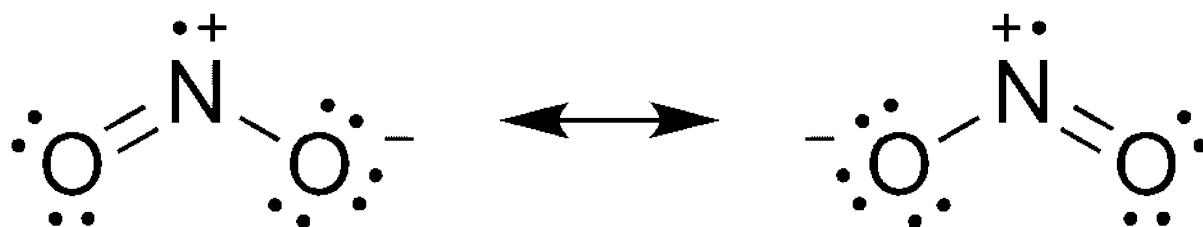
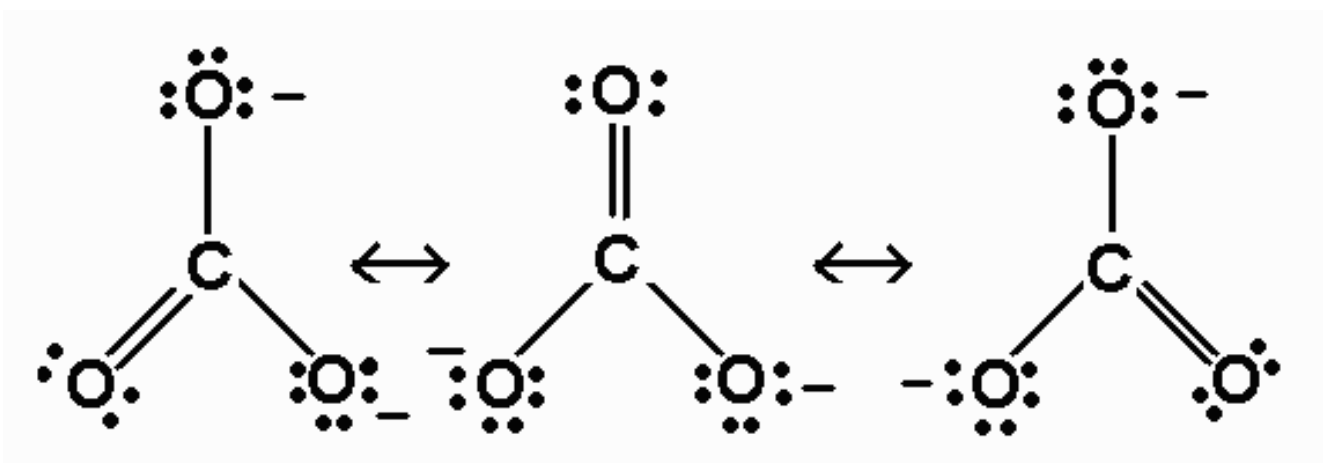


Question 36

- The outermost **s-block** electrons in a **transition metal** tend to be **lost** before the d-block electrons do.

Question 40





Question 44

$$\text{pH} = \text{pK}_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

	PERCENTAGE IONIZATION	
pH - pK_a	ACIDS	BASES
-3	0.1	99.9
-2	1	99
-1	10	90
0	50	50
1	90	10
2	99	1
3	99.9	0.1

Question 49

What is the Reaction Quotient?

K	Q
Equilibrium Constant	Reaction Quotient
Expression is ratio of products to reactants with balanced equation coefficients as powers	Expression is ratio of products to reactants with balanced equation coefficients as powers
Only includes gases and solutions	Only includes gases and solutions
To solve for K, plug in concentrations <u>at equilibrium</u>	To solve for Q, plug in concentrations <u>at any time</u>

Trick: Follow the Direction of the Alligator



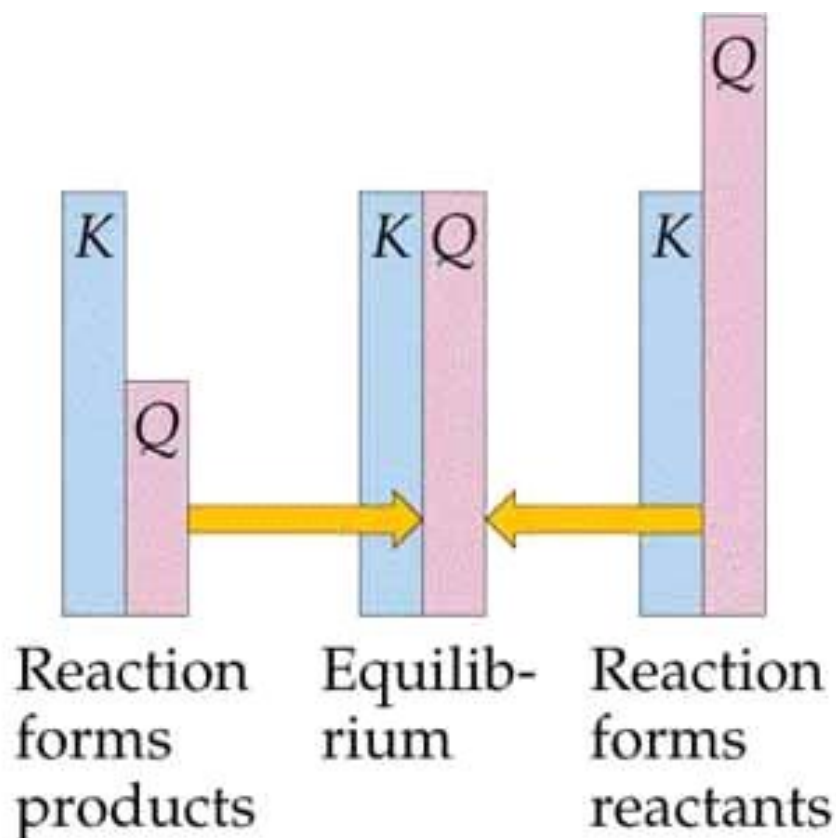
Reaction proceeds to the left!

OR...

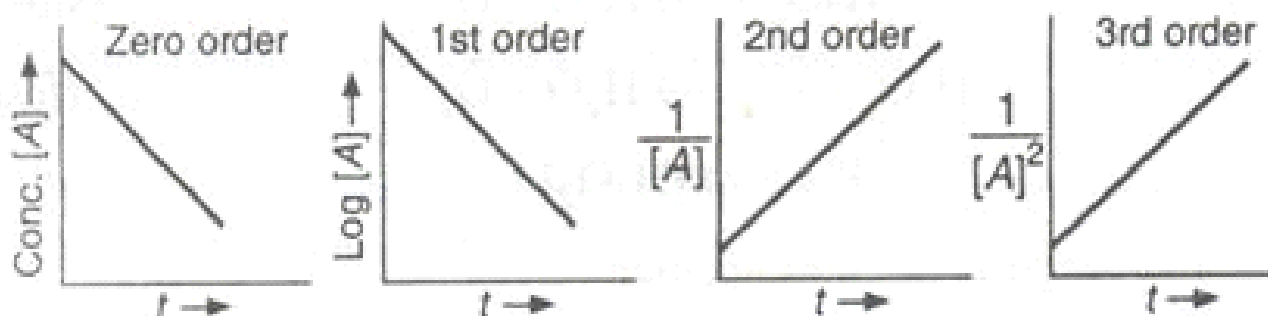


Reaction proceeds to the right!

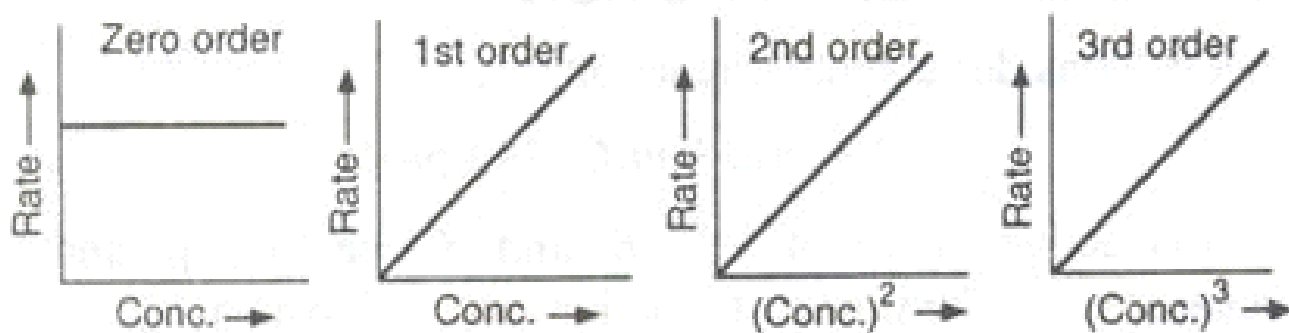
Q



Question 53



(b) Plots from integrated rate equations:



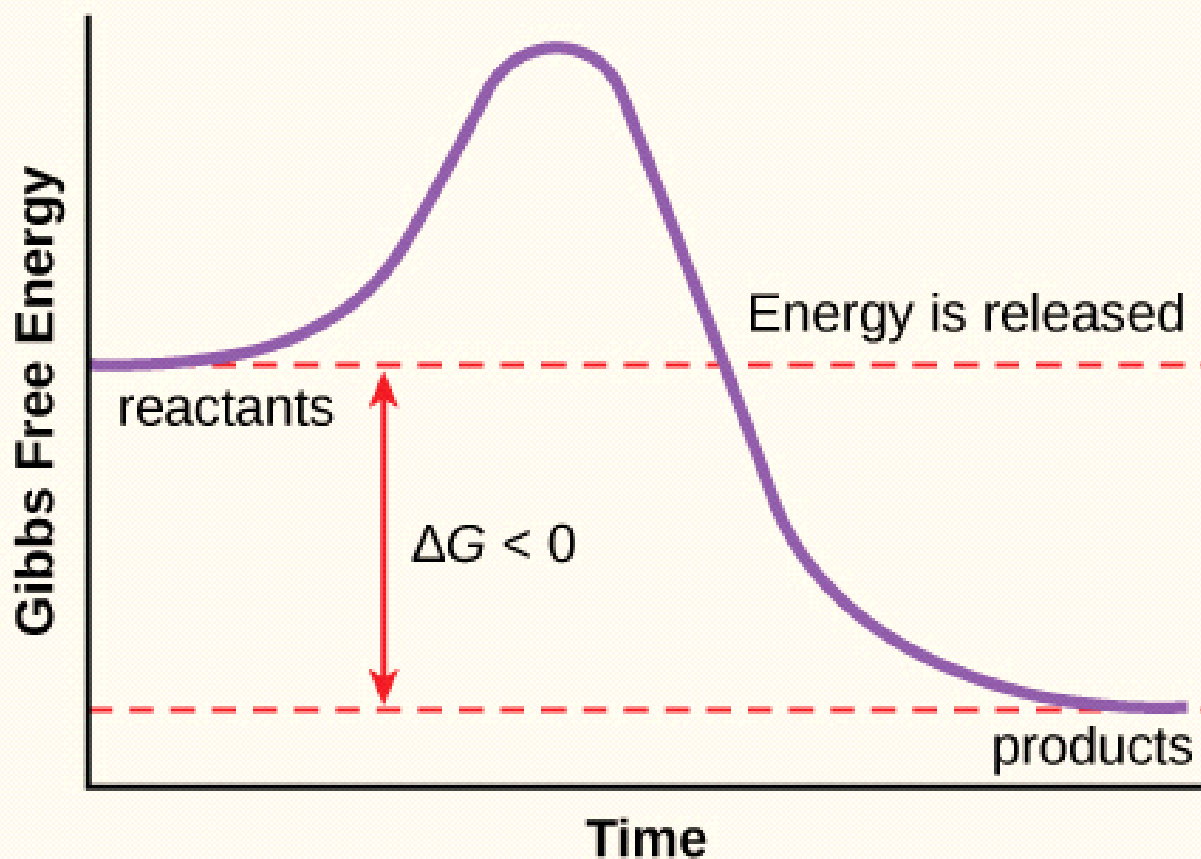
Question 55

- The strength of an atom's **magnetic moment** increases with an increase in the number of **unpaired electrons**.

Question 60

EXERGONIC REACTION: $\Delta G < 0$

Reaction is spontaneous



ENDERGONIC REACTION: $\Delta G > 0$

Reaction is not spontaneous

