Exam Review Packet – Student Version

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Directions

Multiple Choice Section

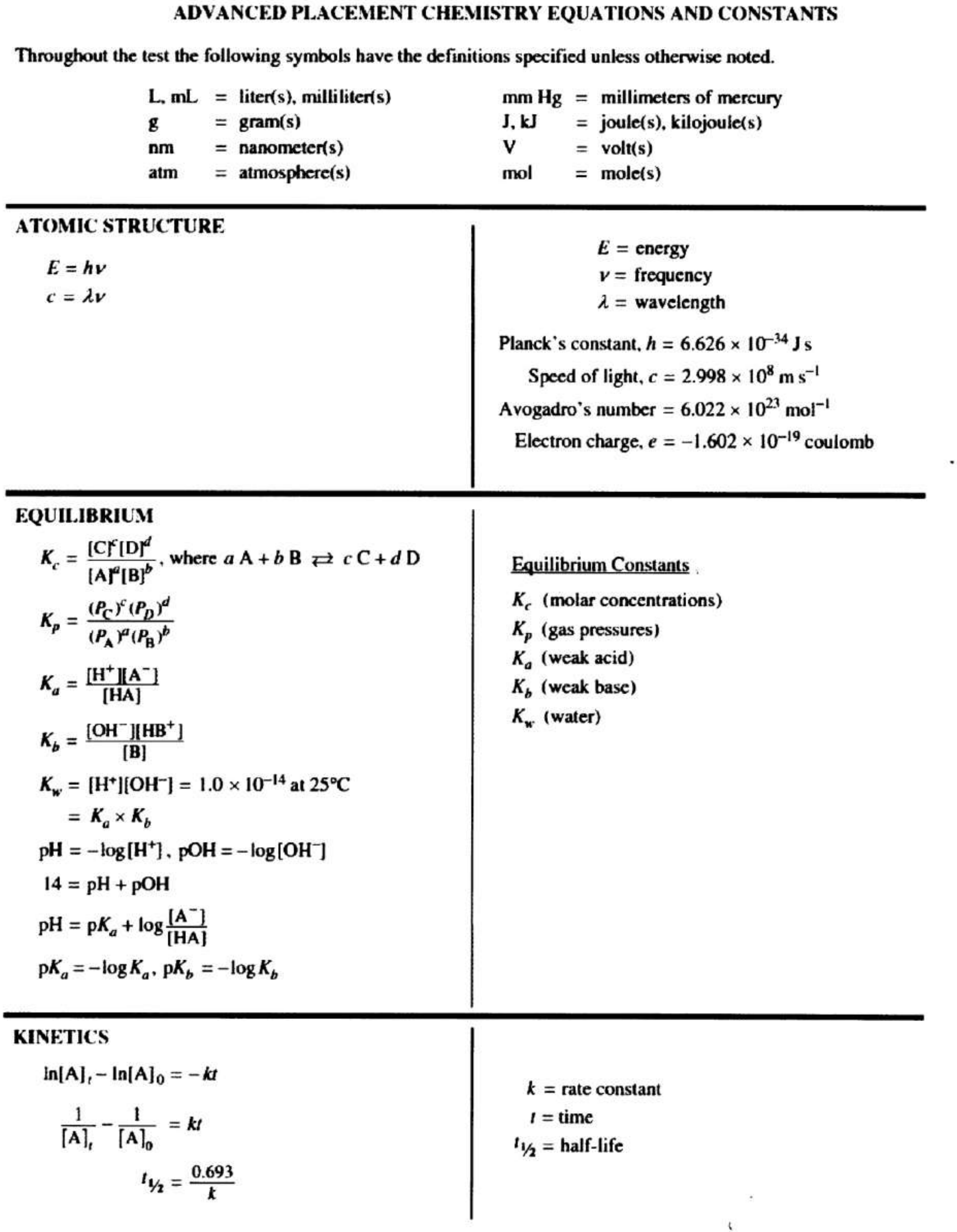
In section 1, there are 60 multiple choice questions. These questions represent the knowledge and skills students should know, understand, and be able to apply. Students will be given a periodic table and an equations and constants list to use during this section.

For all questions, assume that the temperature is 298 K, the pressure is 1.00 atmosphere, and solutions are aqueous unless otherwise specified.

Free Response section

Section II Directions: Questions 1 through 3 are long constructed response questions that should require about 20 minutes to answer. Questions 4 through 7 are short constructed response questions that should require about 7 minutes each to answer. Read each question carefully and write your response in the space provided following each question. Your responses to these questions will be scored on the basis of the accuracy and relevance of the information cited. Explanations should be clear and well organized. Specific answers are preferable to broad, diffuse responses. For calculations, clearly show the method used and the steps involved in arriving at your answers. It is to your advantage to do this, since you may obtain partial credit if you do and you will receive little or no credit if you do not.

Periodic Table and Equations / Constants Sheet



ADVANCED PLACEMENT CHEMISTRY EQUATIONS AND CONSTANTS

Throughout the test the following symbols have the definitions specified unless otherwise noted.

L, mL = liter(s), milliliter(s)
g = gram(s)
nm = nanometer(s)
atm = atmosphere(s)

mm Hg = millimeters of mercury
J, kJ = joule(s), kilojoule(s)
V = volt(s)
mol = mole(s)

ATOMIC STRUCTURE

$$E = h\nu$$

$$c = \lambda\nu$$

E = energy
ν = frequency
λ = wavelength

Planck's constant, $h = 6.626 \times 10^{-34}$ J s
Speed of light, $c = 2.998 \times 10^{8}$ m s^{-1}
Avogadro's number $= 6.022 \times 10^{23}$ mol^{-1}
Electron charge, $e = -1.602 \times 10^{-19}$ coulomb

EQUILIBRIUM

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}, \text{ where } a\,A + b\,B \rightleftarrows c\,C + d\,D$$

$$K_p = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b}$$

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

$$K_b = \frac{[OH^-][HB^+]}{[B]}$$

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ C$$

$$= K_a \times K_b$$

$$pH = -\log[H^+],\ pOH = -\log[OH^-]$$

$$14 = pH + pOH$$

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

$$pK_a = -\log K_a,\ pK_b = -\log K_b$$

Equilibrium Constants

K_c (molar concentrations)
K_p (gas pressures)
K_a (weak acid)
K_b (weak base)
K_w (water)

KINETICS

$$\ln[A]_t - \ln[A]_0 = -kt$$

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

$$t_{1/2} = \frac{0.693}{k}$$

k = rate constant
t = time
$t_{1/2}$ = half-life

GASES, LIQUIDS, AND SOLUTIONS

$$PV = nRT$$

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

$$P_{total} = P_A + P_B + P_C + \ldots$$

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

$$K = °C + 273$$

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

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

Molarity, M = moles of solute per liter of solution

$$A = abc$$

P = pressure
V = volume
T = temperature
n = number of moles
m = mass
M = molar mass
D = density
KE = kinetic energy
v = velocity
A = absorbance
a = molar absorptivity
b = path length
c = concentration

Gas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
$= 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1}$
$= 62.36 \text{ L torr mol}^{-1} \text{ K}^{-1}$
1 atm = 760 mm Hg
= 760 torr
STP = 0.00 °C and 1.000 atm

THERMOCHEMISTRY/ ELECTROCHEMISTRY

$$q = mc\Delta T$$

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

$$\Delta H^\circ = \sum \Delta H_f^\circ \text{ products} - \sum \Delta H_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \sum \Delta G_f^\circ \text{ products} - \sum \Delta G_f^\circ \text{ reactants}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$= -RT \ln K$$
$$= -nFE^\circ$$

$$I = \frac{q}{t}$$

q = heat
m = mass
c = specific heat capacity
T = temperature
S° = standard entropy
H° = standard enthalpy
G° = standard free energy
n = number of moles
E° = standard reduction potential
I = current (amperes)
q = charge (coulombs)
t = time (seconds)

Faraday's constant, F = 96,485 coulombs per mole of electrons

$$1 \text{ volt} = \frac{1 \text{ joule}}{1 \text{ coulomb}}$$

DO NOT DETACH FROM BOOK.

PERIODIC TABLE OF THE ELEMENTS

1 **H** 1.008																	2 **He** 4.00
3 **Li** 6.94	4 **Be** 9.01											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.30											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.06	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.90	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.91	54 **Xe** 131.29
55 **Cs** 132.91	56 **Ba** 137.33	57 ***La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.21	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.08	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.2	83 **Bi** 208.98	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.02	89 **†Ac** 227.03	104 **Rf** (261)	105 **Db** (262)	106 **Sg** (266)	107 **Bh** (264)	108 **Hs** (277)	109 **Mt** (268)	110 **Ds** (271)	111 **Rg** (272)							

*Lanthanide Series	58 **Ce** 140.12	59 **Pr** 140.91	60 **Nd** 144.24	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 151.97	64 **Gd** 157.25	65 **Tb** 158.93	66 **Dy** 162.50	67 **Ho** 164.93	68 **Er** 167.26	69 **Tm** 168.93	70 **Yb** 173.04	71 **Lu** 174.97
†Actinide Series	90 **Th** 232.04	91 **Pa** 231.04	92 **U** 238.03	93 **Np** (237)	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (262)

Big Idea 1: The chemical elements are fundamental building materials of matter, and all matter can be understood in terms of arrangement of atoms. These atoms retain their identity in chemical reactions

Concepts - ATOMIC THEORY, BONDING AND PERIODIC TRENDS

1. Quantum Numbers, electron configurations, Hund's rule, orbital diagrams

2 Trends of the periodic table a) size for atoms and ions b) size of ions c) IE, EA, EN

3. Effective nuclear charge (Z_{eff}) increases as more protons added to same energy level **Z_{eff} is a comparison tool. Coulomb's Law $F=kqq/d^2$**

4. Effective nuclear charge (Z_{eff}) decreases as more shielding electrons are present.

5. When students talk about EN differences they are talking about bonds (within a molecule), we need them to talk about IMF (between molecules)

6. Students often talk about atoms "wanting to gain/lose electrons", being happy, Full, rather than having a stable octet, complete energy level.

7. Correct use of spectroscopy (UV, IR, VIS, PES)

8. Vocabulary

   IE (ionization energy)
   EN (electronegativity)
   EA (electron affinity)

Free Response Questions

1987 Q5

5. Use the details of modern atomic theory to explain each of the following experimental observations.

   a. Within a family such as the alkali metals, the ionic radius increases as the atomic number increases.

   b. The radius of the chlorine atom is smaller than the radius of the chloride ion, Cl^-. (Radii: Cl atom = 0.99 Å; Cl= ion = 1.81 Å)

c. The first ionization energy of aluminum is lower than the first ionization energy of magnesium. (First ionization energies: $_{12}Mg$ = 7.6 ev, $_{13}Al$ = 6.0 ev)

d. For magnesium, the difference between the second and third ionization energies is much larger than the difference between the first and second ionization energies. (Ionization energies, in electron-volts, for Mg: 1st = 7.6, 2nd = 14, 3rd = 80)

1987 Q9

9. Two important concepts that relate to the behavior of electrons in atomic system are the Heisenberg uncertainty principle and the wave-particle duality of matter.

a. State the Heisenberg uncertainty principle as it relates to determining the position and momentum of an object.

b. What aspect of the Bohr theory of the atom is considered unsatisfactory as a result of the Heisenberg uncertainty principle?

c. Explain why the uncertainty principle or the wave nature of particles is not significant when describing the behavior of macroscopic objects, but is very significant when describing the behavior of electrons.

1994 Q9

9. Use principles of atomic structure and/or chemical bonding to answer of each of the following.

a. The radius of the Ca atom is 0.197 nanometers; the radius of the Ca^{2+} ion is 0.099 nanometer. Account for this difference.

b. The lattice energy of CaO(s) is -3,460 kilojoules per mole; the lattice energy for K_2O(s) is -2,240 kilojoules per mole. Account for this difference.

	Ionization Energy	
	First	Second
K	419	3,050
Ca	590	1,140

c. Explain the difference between Ca and K in regard to:

i. their first ionization energies.
ii. their second ionization energies.

Multiple Choice

18. Which of the following elements has the largest first ionization energy?

a. Li
b. Be
c. B
d. C
e. N

22. How many protons, neutrons, and electrons are in an $^{56}_{26}\text{Fe}$ atom?

	Protons	Neutrons	Electrons
a.	26	30	26
b.	26	56	26
c.	30	26	30
d.	56	26	26
e.	56	82	56

23. Which of the following is the electron configuration of an excited atom that is likely to emit a quantum of energy?

a. $1s^2\ 2s^2 2p^6\ 3s^2 3p^1$
b. $1s^2\ 2s^2 2p^6\ 3s^2 3p^5$
c. $1s^2\ 2s^2 2p^6\ 3s^2$
d. $1s^2\ 2s^2 2p^6\ 3s^1$
e. $1s^2\ 2s^2 2p^6\ 3s^1 3p^1$

57. Which of the following lists Mg, P, and Cl in order of increasing atomic radius?

a. Cl < P < Mg
b. Cl < Mg < P
c. Mg < P < Cl
d. Mg < Cl < P
e. P < Cl < Mg

Big Idea 2: Chemical and physical properties of materials can be explained by the structure and arrangement of atoms, ions, or molecules and the forces between them

Concepts - BONDING, LEWIS STRUCTURES AND INTERMOLECULAR FORCES

1. Ionic bonds

2. Covalent bonds, Lewis structures, geometric shapes, bond polarity, molecular polarity, resonance, hybridization, London dispersion forces (LDF), inter vs. intramolecular forces

3. Intermolecular Forces (IMF) are between molecules and help explain differences in FP, BP, solids, liquids, gases, and solubilities.
    a. ion – ion
    b. dipole – dipole with H bonding
    c. dipole – dipole
    d. London dispersion forces (LDF)

4. When students talk about EN differences they are talking about bonds (within a molecule), we need them to talk about IMF (between molecules)

5. Molecular polarity depends on bond polarity and shape of the molecule

6. Vocabulary

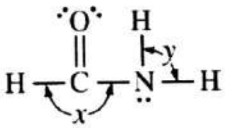
IE (ionization energy)
EN (electronegativity)
EA (electron affinity)

Free Response Questions

2013 Q5

5. Methanamide, CH_3NO, is a liquid at 25 °C.

a. The complete Lewis electron dot diagram for methanamide is shown below.

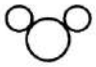


i. In the molecule, angle *x* is not 180°. Estimate the observed angle. Justify your answer.

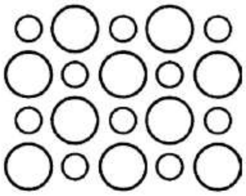
ii. In the molecule, angle *y* is not 90°. Explain why in terms of electron domains (VSEPR model).

b. Consider a molecule with the formula CH_2O_2. The structure of this molecule has a geometry around the carbon atom similar to the geometry around carbon in methanamide. In the box provided below, draw the complete Lewis electron dot diagram for the molecule.

2013 PR Q6



H_2O molecule



LiCl crystal

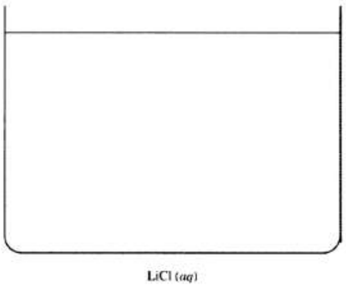
6.

The structures of a water molecule and a crystal of LiCl(s) are represented above. A student prepares a 1.0 M solution by dissolving 4.2 g of LiCl(s) in enough water to make 100 mL of solution.

a. In the space provided below, show the interactions of the components of LiCl(aq) by making a drawing that represents the different particles present in the solution. Base the particles in your drawing on the particles shown in the representations above. Include only one formula unit of LiCl and no more than 10 molecules of water. Your drawing must include the following details.

Identity of ions (symbol and charge)

The arrangement and proper orientation of the particles in the solution

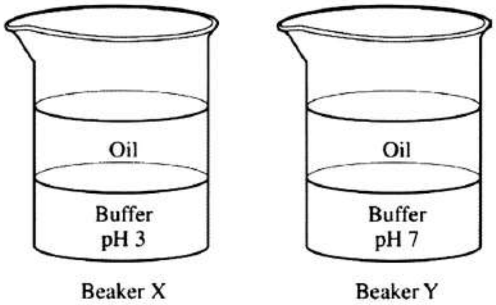


2013 PR Q7

7. $HIn(aq) + H_2O(l)$ ⓧ $In^-(aq) + H_3O^+(aq)$

Yellow blue

The indicator HIn is a weak acid with a pK_a value of 5.0. It reacts with water as represented in the equation above. Consider the two beakers below. Each beaker has a layer of colorless oil (a nonpolar solvent) on top of a layer of aqueous buffer solution. In beaker X the pH of the buffer solution is 3, and in beaker Y the pH of the buffer solution is 7. A small amount of HIn is placed in both beakers. The mixtures are stirred well, and the oil and water layers are allowed to separate.

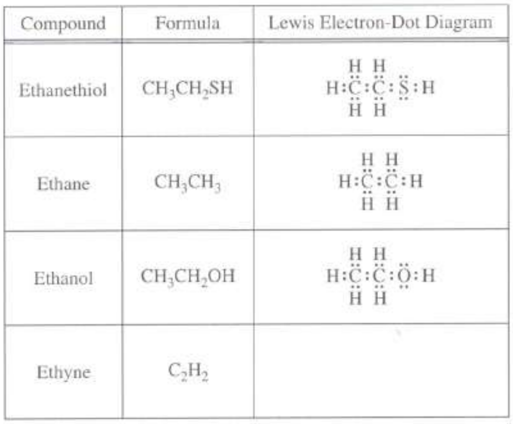


a. What is the predominant form of HIn in the aqueous buffer in beaker Y, the acid form or the conjugate base form? Explain your reasoning.

b. In beaker X the oil layer is yellow, whereas in beaker Y the oil layer is colorless. Explain these observations in terms of both acid-base equilibria and interparticle forces.

2010 Q5

5. Use the information in the table below to respond to the statements and questions that follow. Your answers should be in terms of principles of molecular structure and intermolecular forces.

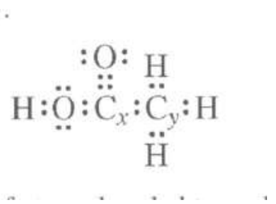


Compound	Formula	Lewis Electron-Dot Diagram
Ethanethiol	CH_3CH_2SH	H H H:C:C:S:H H H
Ethane	CH_3CH_3	H H H:C:C:H H H
Ethanol	CH_3CH_2OH	H H H:C:C:O:H H H
Ethyne	C_2H_2	

a. Draw the complete Lewis electron dot diagram for ethyne in the appropriate cell in the table above.

b. Which of the four molecules contains the shortest carbon-carbon bond? Explain.

c. A Lewis electron dot diagram of a molecule of ethanoic acid is given below. The carbon atoms in the molecule are labeled *x* and *y*, respectively.



Identify the geometry of the arrangement of atoms bonded to each of the following.

i. Carbon *x*

ii. Carbon *y*

d. Energy is required to boil ethanol. Consider the statement “As ethanol boils, energy goes into breaking C-C bonds, C-H bonds, C-O bonds, and O-H bonds.” Is the statement true or false? Justify your answer.

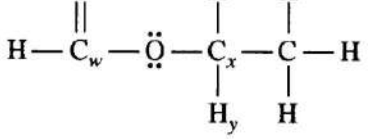
e. Identify a compound from the table above that is nonpolar. Justify your answer.

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.

2011B #6

6. Use principles of molecular structure, intermolecular forces, and kinetic molecular theory to answer the following questions.

a. A complete Lewis electron dot diagram of a molecule of ethyl methanoate is given below.



i. Identify the hybridization of the valence electrons of the carbon atoms labeled C_w.

ii. Estimate the numerical value of the $H_y - C_x - O$ bond angle in an ethyl methanoate molecule. Explain the basis of your estimate.

b. Ethyl methanoate, CH_3CH_2OCHO, is synthesized in the laboratory from ethanol, C_2H_5OH, and methanoic acid, HCOOH, as represented by the following equation.

$C_2H_5OH(l) + HCOOH(l)$ ⓧ $CH_3CH_2OCHO(l) + H_2O(l)$

i. In the box below, draw the complete Lewis electron dot diagram of a methanoic acid molecule.

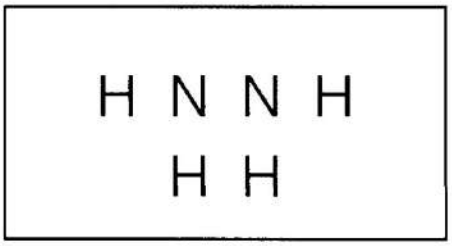
ii. In the box below, draw the complete Lewis electron dot diagrams of a methanoic acid molecule and a water molecule in an orientation that allows a hydrogen bond to form between them.

Hydrogen Bonding between Methanoic Acid and Water

2011 A Q5

5. Hydrazine is an inorganic compound with the formula N_2H_4.

a. In the box below, complete the Lewis electron-dot diagram for the N_2H_4 molecule by drawing in all the electron pairs.



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

c. The normal boiling point of N_2H_4 is 114 ^oC, whereas the normal boiling point of C_2H_6 is -89 ^oC. Explain, in terms of the intermolecular forces present in <u>each</u> liquid, which the boiling point of N_2H_4 is so much higher than that of C_2H_6.

d. Write a balanced chemical equation for the reaction between N_2H_4 and H_2O that explains why a solution of hydrazine in water has a pH greater than 7.

N_2H_4 reacts in air according to the equation below.

$N_2H_4(l) + O_2(g) \rightarrow N_2(g) + 2\ H_2O(g)$ $\Delta H^o = -534$ kJ mol^{-1}

e. Is the reaction an oxidation-reduction, acid-base, or decomposition reaction? Justify your answer.

f. Predict the sign of the entropy change, ΔS, for the reaction. Justify your prediction.

g. Indicate whether the statement written below is true or false. Justify your answer.

The large negative ΔH^o for the combustion of hydrazine results from the large release of energy that occurs when the strong bonds of the reactants are broken.

2012 Q5 (2nd half)

An experiment is performed to compare the solubilities of $I_2(s)$ in different solvents, water and hexane (C_6H_{14}). A student adds 2 mL of H_2O and 2 mL of C_6H_{14} to a test tube. Because H_2O and C_6H_{14} are immiscible, two layers are observed in the test tube. The student drops a small, purple crystal of $I_2(s)$ into the test tube, which is then corked and inverted several times. The C_6H_{14} layer becomes light purple, while the H_2O layer remains virtually colorless.

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.

e. The student then adds a small crystal of $KI(s)$ to the test tube. The test tube is corked and inverted several times. The I^- ion reacts with I_2 to form the I_3^- ion, a linear species.

i. In the box below, draw the complete Lewis electron-dot diagram for the I_3^- ion.

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

Multiple Choice Questions

Questions 4-7 refer to the following species.

a. H_2O
b. NH_3
c. BH_3
d. CH_4
e. SiH_4

4. Has two lone pairs of electrons

5. Has a central atom with less than an octet of electrons

6. Is predicted to have the largest bond angle

7. Has a trigonal-pyramidal molecular geometry

42. Which of the following lists the substances F_2, HCl, and HF in order of increasing boiling point?

a. $HF < HCl < F_2$
b. $HF < F_2 < HCl$
c. $HCl < F_2 < HF$
d. $HCl < HF < F_2$
e. $F_2 < HCl < HF$

47. Which of the following is an isomer of CH_3OCH_3?

a. CH_3CH_3
b. CH_3COOH
c. CH_3CH_2OH
d. $CH_3CH_2CH_3$
e. $CH_3CH_2OCH_2CH_3$

49. Which of the following substances has the greatest solubility in $C_5H_{12}(l)$ at 1 atm?

a. $SiO_2(s)$
b. $NaCl(s)$
c. $H_2O(l)$
d. $CCl_4(l)$
e. $NH_3(g)$

54. High solubility of an ionic solid in water is favored by which of the following conditions?

- I. The existence of strong ionic attractions in the crystal lattice
- II. The formation of strong ion-dipole attractions
- III. An increase in entropy upon dissolving

a. I only
b. I and II only
c. I and III only
d. II and III only
e. I, II, and III

71. Which of the following molecules contains exactly three sigma (σ) bonds and two pi (π) bonds?

a. C_2H_2
b. CO_2
c. HCN
d. SO_3
e. N_2

73. Resonance is most commonly used to describe the bonding in molecules of which of the following?

a. CO_2
b. O_3
c. H_2O
d. CH_4
e. SF_6

Big Idea 3: Changes in matter involve the rearrangement and / or reorganization of atoms and / or the transfer of electrons

Concepts – ELECTROCHEMISTRY

1. oxidation / reduction – balancing equations (review)

2. galvanic cells – {positive, Red Cat}

3. electrolytic cells

4. current, charge, Faradays, (voltage / EMF) (amps, coulombs and volts – unit problem)

5. cell notation

6. salt bridge – "*balance of charge*" not electron balance,
   Good salt bridge materials are soluble salts, not easily oxidized or reduced, doesn't interfere with given redox reaction, ie complex ion formation or precipitation

7. E° and thermodynamically favored

8. $\Delta G^\circ = - n F E^\circ$

9. $E = E^\circ - (0.059 / n) \log K_c$

10. Vocabulary –
    Anode
    Cathode
    Galvanic
    Voltaic

CONCENTRATION UNITS OF SOLUTIONS / COLLIGATIVE PROPERTIES (conceptual only)

1. Molarity M = mole of solute/ L of solution

2. mole fraction = x_a = mole of a /total moles in solution

3. Δ FP ↓ = $(k_f)(m)(i)$ freezing point depression

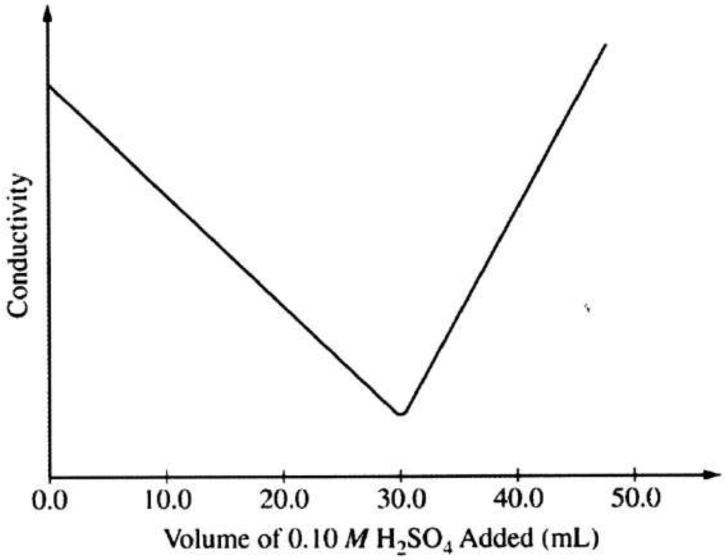
4. Δ BP ↑ = $(k_b)(m)(i)$ boiling point elevation

5. ∏ = (*M*) (*R*) (*T*) (*i*) osmotic pressure

6. Vapor Pressure Lowering = VPL = (x $_{\text{solvent}}$) VP $_{\text{pure solvent}}$
i = Van't Hoff factor
for organic solutes nonelectrolytes *i* = 1
for electrolytes *i* = 2,3,4… NaCl *i* = 2 H_2SO_4 *i* = 3
$AlCl_3$ *i* = 4

Free Response Questions

2013 PR Q1



1.

A student performs an experiment in which the conductivity of a solution of $Ba(OH)_2$ is monitored as the solution is titrated with 0.10 M H_2SO_4. The original volume of the $Ba(OH)_2$ solution is 25.0 mL. A precipitate of $BaSO_4$ ($K_{sp} = 1.0 \times 10^{-10}$) formed during the titration. The data collected from the experiment are plotted in the graph above.

a. As the first 30.0 mL of 0.10 M H_2SO_4 are added to the $Ba(OH)_2$ solution, two types of chemical reactions occur simultaneously. On the lines proved below, write the balanced net ionic equations for (i) the neutralization reaction, and (ii) the precipitation reaction.

i. Equation for neutralization reaction __________________________

ii. Equation for precipitation reaction __________________________

b. The conductivity of the $Ba(OH)_2$ solution decreases as the volume of added 0.10 M H_2SO_4 changes form 0.0 mL to 30.0 mL.

i) Identify the chemical species that enable the solution to conduct electricity as the first 30.0 mL of 0.10 M H_2SO_4 are added.

ii) On the basis of the equations you wrote in part a, explain why the conductivity decreases.

c. Using the information in the graph, calculate the molarity of the original $Ba(OH)_2$ solution.

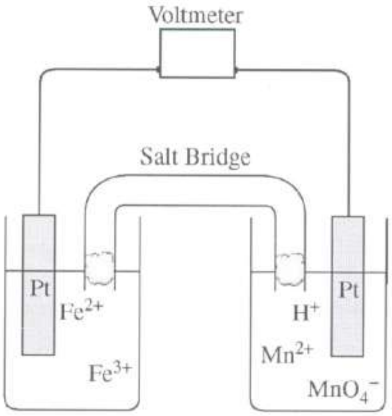
d. Calculate the concentration of $Ba^{2+}(aq)$ in the solution at the equivalence point (after exactly 30.0 mL of 0.10 M H_2SO_4 are added).

e. The concentration of $Ba^{2+}(aq)$ in the solution decreases as the volume of added 0.10 M H_2SO_4 increases from 30.0 mL to 31.0 mL. Explain.

2013 PR Q 6

b. The student passes a direct current through the solution and observes that chlorine gas is produced at the anode. Identify the chemical species produced at the cathode and justify your answer using the information given in the table below.

Half reaction	Standard reduction potential at 25 °C (V)
$Li^+(aq) + e^- \rightarrow Li(s)$	-3.05
$2\ H_2O(l) + 2\ e^- \rightarrow H_2(g) + 2\ OH^-(aq)$	-0.83



2010 B Q2.

$5\ Fe^{2+}(aq) + MnO_4^-(aq) + 8\ H^+(aq) \rightarrow 5\ Fe^{3+}(aq) + Mn^{2+}(aq) + 4\ H_2O(l)$

A galvanic cell and the balanced equation for the spontaneous cell reaction are shown above. The two reduction half reactions for the overall reaction that occurs in the cell are shown in the table below.

Half reaction *E*° (V) at 298 K

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ + 0.77 V

$MnO_4^-(aq) + 8\ H^+(aq) + 5\ e^- \rightarrow Mn^{2+}(aq) + 4\ H_2O(l)$ + 1.49

a. On the diagram, clearly label the cathode.

b. Calculate the value of the standard potential, E^o, for the spontaneous cell reaction.

c. How many moles of electrons are transferred when 1.0 mol of $MnO_4^-(aq)$ is consumed in the overall cell reaction?

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.

Three solutions, one containing $Fe^{2+}(aq)$, one containing $MnO_4^-(aq)$ and one containing $H^+(aq)$, are mixed in a beaker and allowed to react. The initial concentrations of the species in the mixture are 0.60 M $Fe^{2+}(aq)$, 0.10 M $MnO_4^-(aq)$, and 1.0 M $H^+(aq)$.

e. When the reaction mixture has come to equilibrium, which species has the higher concentration, $Mn^{2+}(aq)$ or $MnO_4^-(aq)$? Explain.

f. When the reaction mixture has come to equilibrium, what are the molar concentrations of $Fe^{2+}(aq)$ and $Fe^{3+}(aq)$?

2012 Q2

2. A sample of a pure, gaseous hydrocarbon is introduced into a previously evacuated rigid 1.00 L vessel. The pressure of the gas is 0.200 atm at a temperature of 127 °C.

a. Calculate the number of moles of the hydrocarbon in the vessel.

b. $O_2(g)$ is introduced into the same vessel containing the hydrocarbon. After the addition of the $O_2(g)$, the total pressure of the gas mixture in the vessel is 1.40 atm at 127 °C. Calculate the partial pressure of $O_2(g)$ in the vessel.

The mixture of the hydrocarbon and oxygen is sparked so that a complete combustion reaction occurs, producing $CO_2(g)$ and $H_2O(g)$. The partial pressures of these gases at 127 °C are 0.600 atm for $CO_2(g)$ and 0.800 atm for $H_2O(g)$. There is $O_2(g)$ remaining in the container after the reaction is complete.

c. Use the partial pressures of $CO_2(g)$ and $H_2O(g)$ to calculate the partial pressure of the $O_2(g)$ consumed in the combustion.

d. On the basis of your answers above, write the balanced chemical equation for the combustion reaction and determine the formula of the hydrocarbon.

e. Calculate the mass of the hydrocarbon that was combusted.

f. As the vessel cools to room temperature, droplets of liquid water form on the inside walls of the container. Predict whether the pH of the water in the vessel is less than 7, equal to 7, or greater than 7. Explain your prediction.

Multiple Choice Questions

2013

1. Contains an element in a +1 oxidation state

a. CO_2
b. PbO_2
c. CaO
d. N_2O_5
e. Cu_2O

Questions 8-9 refer to the chemical reactions represented below.

a. $2\ C_6H_6(l) + 15\ O_2(g) \rightarrow 12\ CO_2(g) + 6\ H_2O(l)$

b. $C_2H_3O_2^-(aq) + H_3O^+(aq) \rightarrow HC_2H_3O_2(aq) + H_2O(l)$

c. $4\ H^+(aq) + 4\ Co^{2+}(aq) + O_2(g) + 24\ NH_3(aq) \rightarrow 4\ Co(NH_3)_6^{3+}(aq) + 2H_2O(l)$

d. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

e. $2\ H_2O_2(l) \rightarrow O_2(g) + 2\ H_2O(l)$

8. The reaction between a Brønsted-Lowry acid and a Brønsted-Lowry base

9. The reaction in which a single species is both oxidized and reduced

21. $C_3H_8(g) + 5\ O_2(g) \rightarrow 3\ CO_2(g) + 4\ H_2O(l)$

In the reaction represented above, what is the total number of moles of reactants consumed when 1.00 mole of $CO_2(g)$ is produced?

a. 0.33 mol
b. 1.33 mol
c. 1.50 mol
d. 2.00 mol
e. 6.00 mol

25. $H_2 + F_2 \rightarrow 2\ HF$

In the reaction represented above, what mass of HF is produced by the reaction of 3.0×10^{23} molecules of H_2 with excess F_2? (Assume the reaction goes to completion).

a. 1.0 g
b. 4.0 g
c. 10. g
d. 20. g
e. 40. g

41. … $LiHCO_3(aq)$ + … $H_2SO_4(aq) \rightarrow$ … $Li_2SO_4(aq) + H_2O(l)$ + … $CO_2(g)$

When the equation above is balanced and the coefficients are reduced to lowest whole number terms, what is the coefficient of $H_2O(l)$?

a. 1
b. 2
c. 3
d. 4
e. 5

44. When a 3.22 g sample of an unknown hydrate of sodium sulfate, $Na_2SO_4 \cdot xH_2O(s)$, is heated, H_2O (molar mass 18 g) is driven off. The mass of the anhydrous $Na_2SO_4(s)$ (molar mass 142 g) that remains is 1.42 g. The value of x in the hydrate is

a. 0.013
b. 1.8
c. 6.0
d. 10.
e. 20.

53. What is the empirical formula of an oxide of chromium that is 48 percent oxygen by mass?

a. CrO
b. CrO_2
c. CrO_3
d. Cr_2O
e. Cr_2O_3

63. $2\ MnO_4^-(aq) + 5\ C_2O_4^{2-}(aq) + 16\ H^+(aq) \rightarrow 2\ Mn^{2+}(aq) + 10\ CO_2(g) + 8\ H_2O(l)$

Permanganate and oxalate ions react in an acidified solution according to the balanced equation above. How many moles of $CO_2(g)$ are produced when 20. mL of acidified 0.20 M $KMnO_4$ solution is added to 50. mL of 0.10 M $Na_2C_2O_4$ solution?

a. 0.0040 mol
b. 0.0050 mol
c. 0.0090 mol
d. 0.010 mol
e. 0.020 mol

69. Which of the following is NOT an accepted name for the formula given?

a. CH_3OH .. methanol
b. CuO .. copper (I) oxide
c. $FeCl_3$ .. iron (III) chloride
d. H_2SO_4 .. sulfuric acid
e. $SrCO_3$ .. strontium carbonate

74. A student prepares a solution by dissolving 60.00 g of glucose (molar mass 180.2 g mol^{-1}) in enough distilled water to make 250.0 mL of solution. The molarity of the solution should be reported as

a. 12.01 M
b. 12.0 M
c. 1.332 M
d. 1.33 M
e. 1.3 M

Big Idea 4: Rates of chemical reactions are determined by details of the molecular collisions

Concepts List – KINETICS

1. Rate definition

2. Factors affecting rate

   a. [C]
   b. ΔT
   c. catalysis
   d. surface area
   e. nature of reactants – distinguish between homo- and heterogenous
      i. solids ii. Liquids iii. gases iv. Ions (solutions)

3. Collision theory – orientation and energy

4. Mechanism – relationship between ΔT, ΔS, ΔH – catalysis

5. Orders Rate Law – differential versus integrated
   a. determined by
      i. experimental comparison (20% or less)
      ii. graphing (80% or more)
   b. zero, first, second – determining % remaining and/or % reacted
      ex. $\text{Ln}\ (x_2/x_1) = kt$

6. Rate constants with units (units change with reaction order)
   a. unsuccessful versus effective collisions
   b. orientation and energy

7. Vocabulary

   Reactants vs. products vs. catalyst vs. reaction intermediate

8. Mechanisms are consistent if:

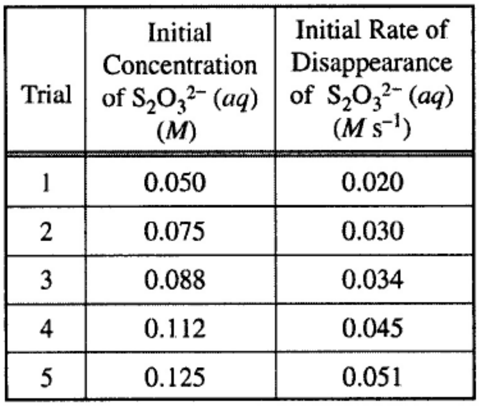
   - steps add up to balanced equation
   - slow step of mechanism will define the mechanistic rate law and rate law expression
   - no reaction intermediates in final rate law expression for comparison with the experimental rate law expression

Free Response Questions

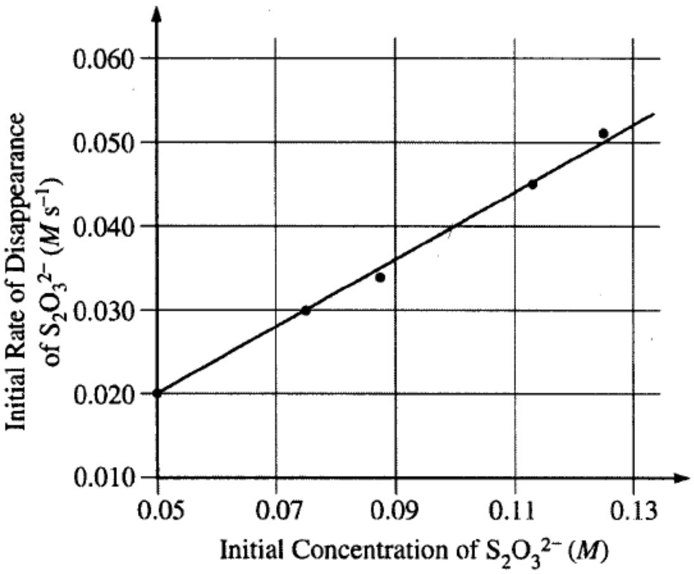
2009B Q2

2. $S_2O_3^{2-}(aq) \rightarrow SO_3^{2-}(aq) + S(s)$ in acidic solution

A student performed an experiment to investigate the decomposition of sodium thiosulfate, $Na_2S_2O_3$, in acidic solution, as represented by the equation above. In each trial the student mixed a different concentration of sodium thiosulfate with hydrochloric acid at constant temperature and determined the rate of disappearance of $S_2O_3^{2-}(aq)$. Data from five trials are given below in the table on the left and are plotted in the graph on the right.



Trial	Initial Concentration of $S_2O_3^{2-}(aq)$ (M)	Initial Rate of Disappearance of $S_2O_3^{2-}(aq)$ ($M\ s^{-1}$)
1	0.050	0.020
2	0.075	0.030
3	0.088	0.034
4	0.112	0.045
5	0.125	0.051



a. Identify the independent variable in the experiment.

b. Determine the order of the reaction with respect to $S_2O_3^{2-}$. Justify your answer by using the information above.

c. Determine the value of the rate constant, *k*, for the reaction. Include units in your answer. Show how you arrived at your answer.

d. In another trial the student mixed 0.10 M $Na_2S_2O_3$ with hydrochloric acid. Calculate the amount of time it would take for the concentration of $S_2O_3^{2-}$ to drop to 0.020 M.

e. On the graph above, sketch the line that shows the results that would be expected if the student repeated the five trials at a temperature lower than that during the first set of trials.

2013 PR Q4

4. $2\ NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$

It is proposed that the reaction represented above proceeds via the mechanism represented by the two elementary steps shown below.

Step I: $NO_2 + F_2 \rightarrow NO_2F + F$ slow

Step II: $NO_2 + F$ ⓧ NO_2F fast reversible

a. Step I of the proposed mechanism involves the collision between NO_2 and F_2 molecules. This step is slow even though such collisions occur very frequently in a mixture of $NO_2(g)$ and $F_2(g)$. Consider a specific collision between a molecule of NO_2 and a molecule of F_2.

i. One factor that affects whether the collision will result in a reaction is the magnitude of the collision energy. Explain

ii. Identify and explain one other factor that affects whether the collision will result in a reaction.

b. Consider the following potential rate laws for the reaction. Circle the rate law below that is consistent with the mechanism proposed above. Explain the reasoning behind your choice in terms of the details of the elementary steps of the mechanism.

Rate = $k\ [NO_2]^2[F_2]$ rate = $k\ [NO_2]\ [F_2]$

2012B #5

5. $2\ H_2O_2(aq) \rightarrow 2\ H_2O(l) + O_2(g)$

The decomposition of hydrogen peroxide to form water and oxygen gas is represented by the equation above. A proposed mechanism for the reaction, which involves the free radicals, HO• and HOO•, is represented by the three equations below.

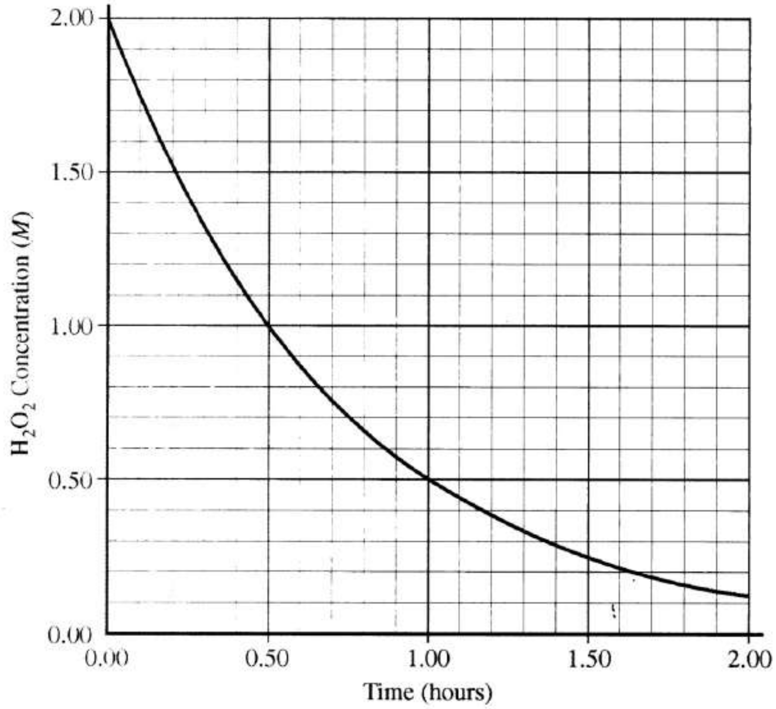
$H_2O_2 \rightarrow 2OH\bullet$ slow

$H_2O_2 + OH\bullet \rightarrow H_2O + HOO\bullet$ fast

$HOO\bullet + OH\bullet \rightarrow H_2O + O_2$ fast

a. Write the rate law consistent with the proposed mechanism above.

b. The rate of the decomposition reaction was studied in an experiment, and the resulting data were plotted in the graph below.



Using the graph, determine the time, in hours, needed for the concentration of H_2O_2 to change from

i. 1.50 M to 0.75 M

ii. 0.80 M to 0.40 M

c. The experimental data are consistent with the proposed mechanism. Explain

An electrochemical cell based on the decomposition of H_2O_2 can be constructed based on the half-reactions in the table below.

Half-reaction	Standard Reduction Potential, *E*°
$H_2O_2 + 2\ e^- \rightarrow 2\ OH^-$	0.88 V
$O_2 + 2\ H_2O + 2\ e^- \rightarrow H_2O_2 + 2\ OH^-$	- 0.15 V

d. Calculate the value of the standard cell potential, *E*°, for the cell.

e. Indicate whether Δ*G*° for the decomposition reaction is greater than 0, less than 0, or equal to 0. Justify your answer.

f. The decomposition of $H_2O_2(aq)$ is slow at 298 K, but a suitable catalyst greatly increases the rate of the decomposition reaction.

i. Draw a circle around each of the quantities below that has a different value for the catalyzed reaction than for the uncatalyzed reaction.

K_{eq} ΔG^o ΔH^o E_a

ii. For any quantity that you circled above, indicate whether its value is greater or less for the catalyzed reaction than for the uncatalyzed reaction. Explain why.

2010 B Q6 (2nd half)

The gas phase decomposition of nitrous oxide has the following two step mechanism.

Step 1 $N_2O \rightarrow N_2 + O$

Step 2 $O + N_2O \rightarrow N_2 + O_2$

f. Write the balanced equation for the overall reaction

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

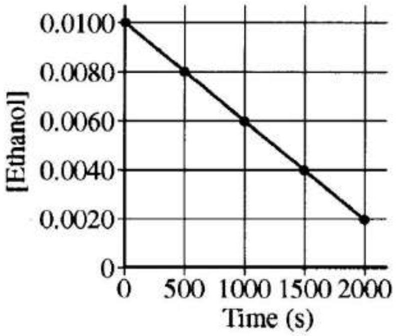
h. Identify the slower step in the mechanism if the rate law for the reaction was determined to be rate = k [N_2O]. Justify your answer

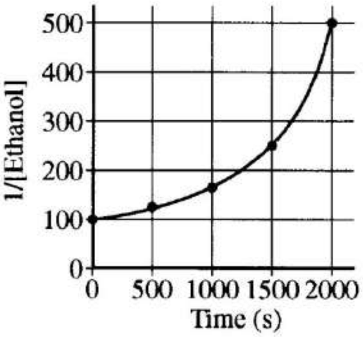
2011 A Q6 (2nd half)

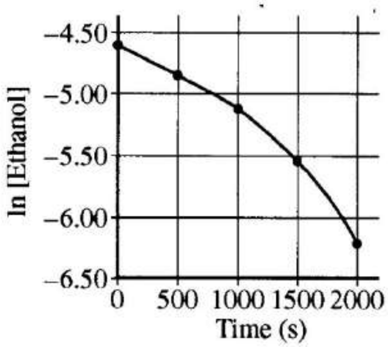
In a second experiment, which is performed at a much higher temperature, a sample of ethanol gas and a copper catalyst are placed in a rigid, empty 1.0 L flask. The temperature of the flask is held constant, and the initial concentration of the ethanol gas is 0.0100 M. The ethanol begins to decompose according to the chemical reaction represented below.

$$CH_3CH_2OH(g) \xrightarrow{Cu} CH_3CHO(g) + H_2(g)$$

The concentration of ethanol gas over time is used to create the three graphs below.







c. Given that the reaction order is zero, one, or two, use the information in the graphs to respond to the following.

i. Determine the order of the reaction with respect to ethanol. Justify your answer.

ii. Write the rate law for the reaction.

iii. Determine the rate constant for the reaction, including units.

d. The pressure in the flask at the beginning of the experiment is 0.40 atm. If the ethanol completely decomposes, what is the final pressure in the flask?

2011 B Q3 (2nd half)

An experiment is carried out to measure the rate of the reaction, which is first order. A 4.70 x 10^{-3} mol sample of $CH_3CH_2NH_2$ is placed in a previously evacuated 2.00 L container at 773 K. After 20.0 minutes, the concentration of the $CH_3CH_2NH_2$ is found to be 3.60 x 10^{-4} mol/L.

d. Calculate the rate constant for the reaction at 773 K. Include units with your answer.

e. Calculate the initial rate, in M min^{-1}, of the reaction at 773 K.

f. If $\frac{1}{[CH_3CH_2NH_2]}$ is plotted versus time for this reaction, would the plot result in a straight line or would it result in a curve? Explain your reasoning.

Multiple Choice Questions

$$C_2H_4(g) + H_2\text{platinium}C_2H_6(g)$$

32. $C_2H_4(g)$ is reduced by $H_2(g)$ in the presence of a solid platinum catalyst, as represented by the equation above. Factors that could affect the rate of the reaction include which of the following?

I. Changes in the partial pressure of $H_2(g)$
II. Changes in the particle size of the platinum catalyst
III. Changes in the temperature of the reaction system

a. III only b. I and II only c. I and III only d. II and III only
e. I, II, and III

Experiment	Initial [*X*] (mol L^{-1})	Initial [Y] (mol L^{-1})	Initial Rate of Formation of Z (mol L^{-1} s^{-1})
1	0.10	0.30	4.0×10^{-4}
2	0.20	0.60	1.6×10^{-3}
3	0.20	0.30	4.0×10^{-4}

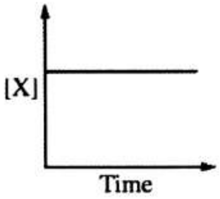
51. The data in the table above were obtained for the reaction $X + Y \rightarrow Z$. Which of the following is the rate law for the reaction?
    a. Rate = $k[X]^2$
    b. Rate = $k[Y]^2$
    c. Rate = $k[X][Y]$
    d. Rate = $k[X]^2[Y]$
    e. Rate = $k[X][Y]^2$

61. If the oxygen isotope ^{20}O has a half-life of 15 seconds, what fraction of a sample of pure ^{20}O remains after 1.0 minute?
    a. 1/2
    b. 1/4
    c. 7/30
    d. 1/8
    e. 1/16

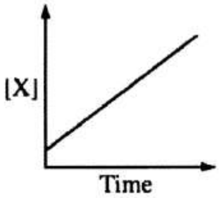
$$X \rightarrow \text{products}$$

62. Pure substance X decomposes according to the equation above. Which of the following graphs indicates that the rate of decomposition is second order in X ?

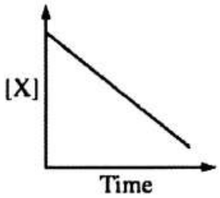
(A)



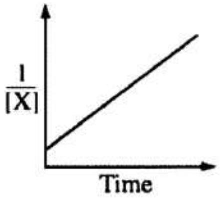
(B)



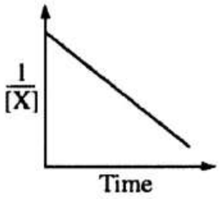
(C)



(D)



(E)



67. The role of a catalyst in a chemical reaction is to

a. decrease the amount of reactants that must be used
b. lower the activation energy for the reaction
c. supply the activation energy required for the reaction to proceed
d. increase the amounts of products formed at equilibrium
e. increase the entropy change for the reaction

Big Idea 5: The laws of thermodynamics describe the essential role of energy and explain and predict the direction of changes in matter

Concepts – THERMODYNAMICS

1. $\Delta H^0{}_{rxn} = \sum \Delta H_f{}^0\text{Products} - \sum\Delta H_f{}^0 \text{ Reactants}$

   $= \sum$ Bond Energy Reactants - $\sum$ Bond energy Products

   ΔH_{rxn} - exothermic **ΔH_{rxn} + endothermic**

2. $\Delta S^0{}_{rxn} = \sum S_f{}^0 \text{ Products} - \sum S_f{}^0 \text{ Reactants}$

   $\Delta S^0{}_{rxn}$ - ordered **$\Delta S^0{}_{rxn}$ + disordered**

3. $\Delta G^0{}_{rxn} = \Delta H^0{}_{rxn} - T\,\Delta S^0{}_{rxn}$

   $\Delta G^0{}_{rxn}$ - thermodynamically favored
   $\Delta G^0{}_{rxn}$ + thermodynamically unfavored

4. $\Delta G^0{}_{rxn} = -RT \ln Q$ $Q = K_{eq}$ free energy and equilibrium

5. $\Delta G^0{}_{rxn} = -nF\,E^0$ free energy and electrochemistry

   F = 96,500 coulombs / mole electrons
   Faraday's constant

6. Phase diagrams

7. $\Delta H_{rxn} = q = m\ (c)\ (\Delta T)$

Free Response Questions

2013 Q2

2. A student is given the task of determining the enthalpy of reaction for the reaction between HCl(aq) and NaOH(aq). The following materials are available.

1.00 M HCl(aq)	1.00 M NaOH(aq)	distilled water
2.00 M HCl(aq)	2.00 M NaOH(aq)	goggles
Insulated cups with covers	gloves	lab coat

Thermometer (± 0.1 °C)   stirring rod

The student may select from the glassware listed in the table below.

Glassware items	Precision
250 mL Erlenmeyer flasks	± 25 mL
100 mL beakers	± 10 mL
100 mL graduated cylinders	± 0.1 mL

a. The student selects two 100 mL beakers, uses them to measure 50 mL each of 1.00 M HCl(aq) solution and 1.00 M NaOH(aq) solution, and measures an initial temperature of 24.5 °C for each solution. Then the student pours the two solutions into an insulated cup, stirs the mixture, covers the cup, and records a maximum temperature of 29.9 °C.

  i. Is the experimental design sufficient to determine the enthalpy of reaction to a precision of two significant figures? Justify your answer.

  ii. List two specific changes to the experiment that will allow the student to determine the enthalpy of reaction to a precision of three significant figures. Explain.

b. A second student is given two solutions, 75.0 mL of 1.00 M HCl and 75.0 mL of 1.00 M NaOH, each at 25.0 °C. The student pours the solutions into an insulated cup, stirs the mixture, covers the cup, and records the maximum temperature of the mixture.

  i. The student calculates the amount of heat evolved in the experiment to be 4.1 kJ. Calculate the student's experimental value for the enthalpy of reaction, in $\text{kJ/mol}_{\text{rxn}}$.

  ii. The student assumes that the thermometer and the calorimeter do not absorb energy during the reaction. Does this assumption result in a calculated value of the enthalpy of reaction that is higher than, lower than, or the same as it would have been had the heat capacities of the thermometer and calorimeter been taken into account? Justify your answer.

  iii. One assumption in interpreting the results of the experiment is that the reaction between HCl(aq) and NaOH(aq) goes to completion. Justify the validity of this assumption in terms of the equilibrium constant for the reaction.

c. A third student calculates a value for the enthalpy of reaction that is significantly higher than the accepted value.

  i. Identify a specific error in procedure made by the student that will result in a calculated value for the enthalpy of reaction that is higher than the accepted value. (Vague statements like “human error” or “incorrect calculations” will not earn credit).

ii. Explain how the error that you identified in part c i) leads to a calculated value for the enthalpy of reaction that is higher than the accepted value.

2012 B Q 3

3. $CaSO_4•2H_2O(s)$ ⓧ $CaSO_4(s) + 2\ H_2O(g)$

The hydrate $CaSO_4•2H_2O(s)$ can be heated to form the anhydrous salt, $CaSO_4(s)$, as shown by the reaction represented above.

a. Using the data in the table below, calculate the value of ΔG^o, in kJ / mol_{rxn}, for the reaction at 298 K.

Substance	ΔG_f^o at 298 K (kJ / mol)
$CaSO_4•2H_2O(s)$	-1795.70
$CaSO_4(s)$	-1320.30
$H_2O(g)$	-228.59

b. Given that the value of ΔH^o for the reaction at 298 K is +105 kJ / mol_{rxn}, calculate the value of ΔS^o for the reaction at 298 K. Include units with your answer.

2009B Q5

5. Answer the following questions about nitrogen, hydrogen, and ammonia.

a. In the boxes below, draw the complete Lewis electron-dot diagrams for N_2 and NH_3.

b. Calculate the standard free energy change, ΔG^o, that occurs when 12.0 g of $H_2(g)$ reacts with excess $N_2(g)$ at 298 K according to the reaction represented below.

$N_2(g) + 3\ H_2(g)$ ⓧ $2\ NH_3(g)$ $\qquad \Delta G_{298}^o = -34\ kJ\ mol^{-1}$

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

d. The value of the standard entropy change, $\Delta S_{298}°$, for the reaction is -199 J mol^{-1} K^{-1}. Explain why the value of $\Delta S_{298}°$ is negative.

e. Assume that $\Delta H°$ and $\Delta S°$ for the reaction are independent of temperature.

   i. Explain why there is a temperature above 298 K at which the algebraic sign of the value of $\Delta G°$ changes.

   ii. Theoretically, the best yields of ammonia should be achieved at low temperatures and high pressures. Explain.

Multiple Choice Questions

2013

29. Which of the following processes involves the greatest increase in entropy?

a. $SO_3(g) + H_2(g) \rightarrow SO_2(g) + H_2O(g)$

b. $N_2(g) + 3\ H_2(g) \rightarrow 2\ NH_3(g)$

c. $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$

d. $C_2H_2(g) + 2\ H_2(g) \rightarrow C_2H_6(g)$

e. $MgSO_3(s) \rightarrow MgO(s) + SO_2(g)$

$$2\ NH_3(g) \rightarrow 3\ H_2(g) + N_2(g)\ \Delta H^o_{298} = 92\ kJ/mol_{rxn}$$

37. According to the information above, what is the standard enthalpy of formation, ΔH_f^o, for $NH_3(g)$ at 298 K ?

a. −92 kJ/mol
b. −46 kJ/mol
c. 46 kJ/mol
d. 92 kJ/mol
e. 184 kJ/mol

46. In an insulated cup of negligible heat capacity, 50. g of water at 40.°C is mixed with 30. g of water at 20.°C. The final temperature of the mixture is closest to

a. 22°C
b. 27°C
c. 30.°C
d. 33°C
e. 38°C

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

52. For the reaction represented above at 25°C, what are the signs of ΔH°, ΔS°, and ΔG° ?

	ΔH^o	ΔS^o	ΔG^o
a.	+	+	+
b.	+	+	-
c.	+	-	-
d.	-	-	-
e.	-	-	+

2012

31. Under which of the following conditions can an endothermic reaction be thermodynamically favorable?

a. ΔG is positive
b. ΔS is negative
c. T ΔS > ΔH
d. TΔS = 0
e. There are no conditions under which an endothermic reaction can be thermodynamically favorable.

53. $$4\ NH_3(g) + 3\ O_2(g) \rightarrow 2\ N_2(g) + 6\ H_2O(g)$$

If the standard molar heats of formation of ammonia, $NH_3(g)$, and gaseous water, $H_2O(g)$, are -46 kJ / mol and -242 kJ / mol, respectively, what is the value of ΔH_{298}^o for the reaction represented above?

a. -190 kJ / mol_{rxn}
b. -290 kJ / mol_{rxn}
c. -580 kJ / mol_{rxn}
d. -1270 kJ / mol_{rxn}
e. -1640 kJ / mol_{rxn}

54. When a magnesium wire is dipped into a solution of lead (II) nitrate, a black deposit forms on the wire. Which of the following can be concluded from this observation?

a. The standard reduction potential, E^o, for $Pb^{2+}(aq)$ is greater than that for $Mg^{2+}(aq)$.

b. Mg(s) is less easily oxidized than Pb(s)

c. An external source of potential must have been supplied.

d. The magnesium wire will be the cathode of a Mg / Pb cell.

e. Pb(s) can spontaneously displace $Mg^{2+}(aq)$ from solution.

Big Idea 6: Any bond or intermolecular attraction that can be formed can be broken. These two processes are in a dynamic competition, sensitive to initial conditions and external perturbations.

Concept List – EQUILIBRIUM

All Problems are equilibrium problems because

All problems involve stoichiometry: soluble salts, strong acids, strong bases
Some problems involve equilibrium: “insoluble” salts, weak acids, weak bases

For chemical reactions – K_{eq}, K_c, and K_p are the important quantities

For physical changes – K_a, K_b, K_{sp}, K_{ionize}, and $K_{dissocation}$ are the important quantities

Important points

1. Law of mass action

   $aA + bB + \ldots$ ⓧ $rR + sS + xxx$

   $K_c = [R]^r\ [S]^s \ldots / [A]^a\ [B]^b \ldots$

2. K_c for molarity for ions and gases

3. K_p with atm, or mmHg for gases

   Relationship / connection between these $K_p = K_c\ (RT)^{\Delta n}$

4. Orientation of collisions

5. Shifting equilibrium – Le Chatlier’s Principle

   a. solid
   b. liquid
   c. catalyst
   d. inert gas added
   e. temperature changes (increasing T favors endothermic processes)
   f. only factors in equation constant will affect K_{eq} eg. $CaCO_3(s)$ ⓧ $CaO(s) + CO_2(g)$
   g. pressure / volume changes

6. Important vocabulary

   Driving force
   Favors (reactants or products)
   Shifts (in LeChatelier arguments)

7. $K > 1$ products favored

   $K < 1$ reactants favored

8. Excluded: solids, pure liquids, water (in aqueous solution)

9. Typical question: Given K_c and the starting concentration of reactants, find the concentration (or pH !) of products at equilibrium.

   Example: K_c of acetic acid = 1.754×10^{-5}. Find the pH of a 0.100 *M* solution of acetic acid.

10. Equilibrium constant for a reverse reaction = 1 / *K* of the value of the forward reaction.

11. When using Hess's Law: $K_{overall} = K_1 \times K_2$

12. If out of equilibrium: Calculate the reaction quotient (*Q*) in a similar fashion to the way an equilibrium constant would be found. If:

    $K > Q$ forward reaction occurs to reach equilibrium

    $K < Q$ reverse reaction occurs to reach equilibrium

13. Problem solving: Learn when to make an approximation (needed for multiple choice and free response questions!). 5% rules usually works when value of *K* is 10^{-2} or smaller than value of known concentrations.

    Example: A ⓧ B + C $K = 3.0 \times 10^{-6}$

    If [A] = 5.0 M; find [C] at equilibrium

    If greater than 5 % use the quadratic equation:

    $ax^2 + bx + c = 0$

    $$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Concept List – ACID – BASE

$pH = -\log[H^+]$ $pOH = -\log[OH^-]$ $K_w = [H^+][OH^-] = 1\times10^{-14}$ at 25 °C

If you know one quantity, you know the other three

$$\begin{tikzcd}
 & pH \arrow[dr, leftrightarrow] & \\
{[H^+]} \arrow[ur, leftrightarrow] \arrow[dr, leftrightarrow] & & pOH \\
 & {[OH^-]} \arrow[ur, leftrightarrow] &
\end{tikzcd}$$

Definitions

Acid	Base	Theory
Donates H^+	Donates OH^-	Arrhenius
Donates protons	Accepts protons - {anions?}	Bronsted – Lowry

Conjugate Acid – Base Pairs

1. $HCl + H_2O \rightarrow H_3O^+ + Cl^-$

2. $NH_3 + H_2O$ ⓧ $NH_4^+ + OH^-$

3. $HSO_4^- + H_2O$ ⓧ $H_3O^+ + SO_4^{2-}$

4. $CO_3^{2-} + H_3O^+$ ⓧ $HCO_3^- + H_2O$

A. K_a Weak Acid HCN ⓧ $H^+ + CN^-$

$$K_a = \frac{[H^+][CN^-]}{[HCN]} = 6.2 \times 10^{-10}$$

What is the pH of a 0.5 *M* HCN solution?

B. K_b Weak base $NH_3 + H_2O$ ⓧ $NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

What is the pH of a 0.5 *M* NH_2OH solution?

C. K_{sp} Insoluble Salts $MgF_2(s)$ ⓧ $Mg^{2+} + 2F^-$

$K_{sp} = [Mg^{2+}] [F^-]^2 = 6.6 \times 10^{-9}$

What is the solubility of MgF_2 in molarity?

D. **Buffers** – a weak acid/base and its soluble salt (conjugate base or acid) mixture

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{base}]}{[\mathrm{acid}]}$$

What is the pH of a 0.5 *M* $HC_2H_3O_2$ in 2 *M* $NaC_2H_3O_2$ solution? $K_a = 1.8 \times 10^{-5}$

E. Salts of Weak Acids and Weak Bases

What is the pH of a 1 *M* $NaC_2H_3O_2$ solution?

Titrations and Endpoints

At endpoint: acid moles = base moles or $[H^+] = [OH^-]$

Strong acid – strong base	**endpoint pH = 7**
Strong acid – weak base	**endpoint pH < 7**
Weak acid – strong base	**endpoint pH > 7**

The last two are important because of conjugate acid and base pairs

11. Acid strength – know the 6 strong acids: HCl, HBr, HI, HNO_3, $HClO_4$, and H_2SO_4 (removal of the first H^+ only)

a) binary acids – acid strength increased with increasing size and electronegativity of the "other element". (NOTE: Size predominates over electronegativity in determining acid strength.)

Example: $H_2Te > H_2O$ and $HF > NH_3$

b) oxoacids – Acid strength increases with increasing:

1) electronegativity
2) number of bonded oxygen atoms
3) oxidation state

of the “central atom”. However, need to show as electron withdrawing groups rather than trends (trends need to be explained as a result of chemical principles rather than solely as a trend).

Example: $HClO_4$ $[O_3Cl(OH)]$ is very acidic
NaOH is very basic

Acid strength also increases with DECREASING radii of the “central atom”

Example: HOCl (bond between Cl and OH is covalent – acidic)
HOI (bond between I and OH is ionic – basic)

12. Acid Ionization Constant (K_a):

$HA + H_2O$ ⓧ $H_3O^+ + A^-$

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

Example: $HF + H_2O$ ⓧ $H_3O^+ + F^-$

$$K_a = \frac{[F^-][H_3O^+]}{[HF]}$$

What is the pH of 0.5 *M* HCN solution for which $K_a = 6.2 \times 10^{-10}$?

13. Base Ionization Constant (K_b):

$B + H_2O$ ⓧ $BH^+ + OH^-$

$$K_b = \frac{[BH^-][OH^-]}{[B]}$$

Example: $F^- + H_2O$ ⓧ $HF + OH^-$

$$K_b = \frac{[HF][OH^-]}{[F^-]}$$

What is the pH of a 0.5 *M* NH_2OH solution for which $K_b = 6.6 \times 10^{-9}$?

Do equal number of K_a and K_b problems as they are equally likely!

14. **$K_a \times K_b = K_w = 10^{-14}$ for conjugate acid/base pairs @ 25 °C!**

15. Percent ionization = $[H^+]_{\text{equilibrium}} / [HA]_{\text{initial}} \times 100$

16. **Buffers:**

Similar concentrations of a weak acid and its conjugate base
-or-

Similar concentrations of a weak base and its conjugate acid

If these concentrations are large in comparison to SMALL amounts of added acid or base, equilibrium will be shifted slightly and the pH change resisted. Consider:

HA ⓧ $H^+ + A^-$

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

$[H^+] = K_a\ [HA] / [A^-]$

$pH = pK_a - \log [HA] / [A^-]$ or $pH = pK_a + \log [A^-] / [HA]$
(Henderson-Hasselbach equation)

$B + H_2O$ ⓧ $HB^+ + OH^-$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$[OH^-] = K_b\ [B] / [HB^+]$ or $pOH = pK_b + \log [HB^+]/[B]$
(Henderson-Hasselbach equation)

What is the pH of a solution which is 0.5 *M* $HC_2H_3O_2$ in 2 *M* $NaC_2H_3O_2$ for which $K_a = 1.8 \times 10^{-5}$?

17. Polyprotic Acids: H_3PO_4, H_2SO_4, $H_2C_2O_4$, etc.

18. Equivalence Point – the point at which stoichiometric amounts of reactants have reacted.

NOTE: This only occurs at pH = 7 for the reaction of a strong acid with a strong base. The equivalence point will occur ABOVE pH = 7 (more basic) for a weak acid / strong base titration. (the conjugate base of the weak acid will react with water.) The equivalence point will occur BELOW pH = 7 for a weak base / strong acid titration (the conjugate acid of the weak base with react with water).

19. Indicators – select bases on the pH at the equivalence point.

20. **Titration curves:**

a) Weak acid / strong base $HA + OH^-$ ⓧ $A^- + H_2O$

NOTE: Graph should have “pH” as the vertical axis and “added base” as the horizontal axis. The graph should be in an “S” shape. The middle of the lower part of the “S” indicates the point of maximum buffering where $[HA] / [A^-] = 1$. The middle of the “S” is the equivalence point (above pH = 7) and $[HA] = 0$. The top part of the “S” levels off at the pH of the base solution.

b) Weak base / strong acid $B + H_3O^+$ ⓧ $BH^+ + H_2O$

NOTE: Graph should have “pH” as the vertical axis and “added base” as the horizontal axis. The graph should be in a “backwards S” shape. The middle of the upper part of the “backwards S” indicates the point of maximum buffering where $[B] / [HB^+] = 1$. The middle of the “backwards S” is the equivalence point (below pH = 7) and $[B] = 0$. The bottom part of the “backwards S” levels off at the pH of the acid solution.

c) Weak diprotic acid / strong base $H_2A + OH^-$ ⓧ $HA^- + H_2O$

$HA^- + OH^-$ ⓧ $A^{2-} + H_2O$

NOTE: Graph should have “pH” as the vertical axis and “added base” as the horizontal axis. The graph should be in a “double S” shape. The middle of the lower part of the “first S” indicates the point of maximum buffering of the first buffering zone where $[H_2A] / [HA^-] = 1$. The middle of the “first S” is the first equivalence point where $[H_2A] = 0$. The top of the “first S” (i.e. the lower part of the “second S”) indicates the point of maximum buffering of the second buffering zone where $[HA^-] / [A^{2-}] = 1$. The middle of the “second S” is the second equivalence point where $[HA^-] = 0$. The top part of the “second S” levels off at the pH of the base solution.

21. **Solubility Product (K_{sp})**

Example 1: $Co(OH)_2(s)$ ⓧ $Co^{2+} + 2OH^-$ $K_{sp} = [Co^{2+}][OH^-]^2$
(don’t forget – molar concentration of OH^- is twice the solubility)

Example 2: Solubility of Ag_2SO_4 is 0.016 mol L^{-1} (5.0 g L^{-1}). Find the K_{sp} of Ag_2SO_4. (Answer: $K_{sp} = 1.5 \times 10^{-5}$)

22. **Ion product (Q_i) – equivalent to the “reaction quotient”**

$K_{sp} > Q_i$ all ions in solution; more solid will dissolve
$Q_i = K_{sp}$ equilibrium – solution is saturated
$K_{sp} < Q_i$ precipitation will occur until $Q_i = K_{sp}$

Free Response Questions

2013 PR Q3

3. $SO_2Cl_2(g)$ ⓧ $SO_2(g) + Cl_2(g)$

A 4.32 g sample of liquid SO_2Cl_2 is placed in a rigid, evacuated 1.50 L reaction vessel. As the container is heated to 400. K, the sample vaporizes completely and starts to decompose according to the equation above. The decomposition reaction is endothermic.

a. If no decomposition occurred, what would be the pressure, in atm, of the $SO_2Cl_2(g)$ in the vessel at 400. K?

b. When the system has reached equilibrium at 400. K, the total pressure in the container is 1.26 atm. Calculate the partial pressures, in atm of $SO_2Cl_2(g)$, $SO_2(g)$, and $Cl_2(g)$ in the container at 400. K.

c. For the decomposition reaction at 400. K,

i. write the equilibrium constant expression for K_p for the reaction, and

ii. calculate the value of the equilibrium constant, K_p.

d. The temperature of the equilibrium mixture is increased to 425 K. Will the value of K_p increase, decrease, or remain the same? Justify your prediction.

e. In another experiment, the original partial pressures of $SO_2Cl_2(g)$, $SO_2(g)$, and $Cl_2(g)$ are 1.0 atm each at 400. K. Predict whether the amount of $SO_2Cl_2(g)$ in the container will increase, decrease, or remain the same. Justify your prediction.

2010B #1

1. The compound butane, C_4H_{10}, occurs in two isomeric forms, *n*-butane and isobutane (2-methyl propane). Both compounds exist as gases at 25 °C and 1.0 atm.

a. Draw the structural formula of each of the isomers (include all atoms). Clearly label each structure.

b. On the basis of molecular structure, identify the isomer than has the higher boiling point. Justify your answer.

The two isomers exist in equilibrium as represented by the equation below.

n-butane(g) ⓧisobutane(g) $K_c = 2.5$ at 25 °C

Suppose that a 0.010 mol sample of pure *n*-butane is placed in an evacuated 1.0 L rigid container at 25 °C.

c. Write the expression for the equilibrium constant, K_c, for the reaction.

d. Calculate the initial pressure in the container when the *n*-butane is first introduced (before the reaction starts).

e. The *n*-butane reacts until equilibrium has been established at 25 °C.

  i. Calculate the total pressure in the container at equilibrium. Justify your answer.

  ii. Calculate the molar concentration of each species at equilibrium.

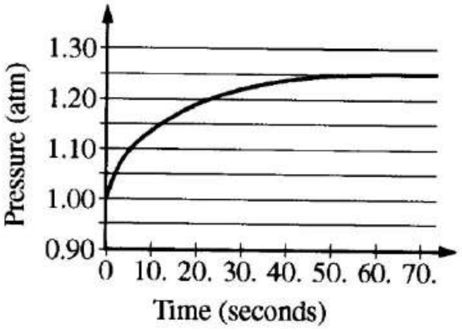
  iii. If the volume of the system is reduced to half of its original volume, what will the new concentration of *n*-butane after equilibrium has been reestablished at 25 °C? Justify your answer.

Suppose that in another experiment a 0.010 mol sample of pure isobutane is placed in an evacuated 1.0 L rigid container and allowed to come to equilibrium at 25 °C.

e. Calculate the molar concentration of each species after equilibrium has been established.

2011 B Q 6

c. A small amount of liquid ethyl methanoate (boiling point 54 °C) was placed in a rigid closed 2.0 L container containing argon gas at an initial pressure of 1.00 atm and a temperature of 20 °C. The pressure in the container was monitored for 70. seconds after the ethyl methanoate was added, and the data in the graph below were obtained. It was observed that some liquid ethyl methanoate remained in the flask after 70.0 seconds. (Assume that the volume of the remaining liquid is negligible compared to the total volume of the container.)



  i. Explain why the pressure in the flask increased during the first 60. seconds.

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

iii. What is the value of the partial pressure of ethyl methanoate vapor in the container at 60. seconds?

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.)

2009 B Q1

1. A pure 14.85 g sample of the weak base ethylamime, $C_2H_5NH_2$, is dissolved in enough water to make 500. mL of solution.

a. Calculate the molar concentration of the $C_2H_5NH_2$ in the solution.

The aqueous ethylamine reacts with water according to the equation below.

$C_2H_5NH_2(aq) + H_2O(l)$ ⓧ $C_2H_5NH_3^+(aq) + OH^-(aq)$

b. Write the equilibrium constant expression for the reaction between $C_2H_5NH_2(aq)$ and water.

c. Of $C_2H_5NH_2(aq)$ and $C_2H_5NH_3^+(aq)$, which is present in the solution at the higher concentration at equilibrium? Justify your answer.

d. A different solution is made by mixing 500. mL of 0.500 M $C_2H_5NH_2$ with 500. mL of 0.200 M HCl. Assume that volumes are additive. The pH of the resulting solution is found to be 10.93.

i. Calculate the concentration of $OH^-(aq)$ in the solution.

ii. Write the net ionic equation that represents the reaction that occurs when the $C_2H_5NH_2$ solution is mixed with the HCl solution.

iii. Calculate the molar concentration of the $C_2H_5NH_3^+(aq)$ that is formed in the reaction.

iv. Calculate the value of K_b for $C_2H_5NH_2$.

2010 Q1

1. Several reactions are carried out using AgBr, a cream-colored silver salt for which the value of the solubility-product constant, K_{sp}, is 5.0×10^{-13} at 298 K

a. Write the expression for the solubility-product constant, K_{sp}, of AgBr.

b. Calculate the value of $[Ag^+]$ in 50.0 mL of a saturated solution of AgBr at 298 K.

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.

d. Calculate the minimum volume of distilled water, in liters, necessary to completely dissolve a 5.0 g sample of AgBr(s) at 298 K. (The molar mass of AgBr is 188 g mol^{-1}).

e. A student mixes 10.0 mL of 1.5×10^{-4} M $AgNO_3$ with 2.0 mL of 5.0×10^{-4} M NaBr and stirs the resulting mixture. What will the student observe? Justify you answer with calculations.

f. The color of another salt of silver, AgI(s) is yellow. A student adds a solution of NaI to a test tube containing a small amount of solid, cream-colored AgBr. After stirring the contents of the test tube, the student observes that the solid in the test tube changes color from cream to yellow.

  i. Write the chemical equation for the reaction that occurred in the test tube.

  ii. Which salt has the greater value of K_{sp}: AgBr or AgI? Justify your answer.

2011 B Q1

1. Answer the following questions about the solubility and reactions of the ionic compounds $M(OH)_2$ and MCO_3, where M represents an unidentified metal.

a. Identify the charge of the M ion in the ionic compounds above.

b. At 25 °C, a saturated solution of $M(OH)_2$ has a pH of 9.15.

  i. Calculate the molar concentration of $OH^-(aq)$ in the saturated solution.

  ii. Write the solubility product expression for $M(OH)_2$.

  iii. Calculate the value of the solubility product constant, K_{sp}, for $M(OH)_2$ at 25 °C.

c. For the metal carbonate, MCO_3, the value of the solubility product constant, K_{sp}, is 7.4×10^{-14} at 25 °C. On the basis of this information and your results in part b), which compound, $M(OH)_2$ or MCO_3, has the greater molar solubility in water at 25 °C? Justify your answer with a calculation.

d. MCO_3 decomposes at high temperatures, as shown by the reaction represented below.

$MCO_3(s)$ ⓧ $MO(s) + CO_2(g)$

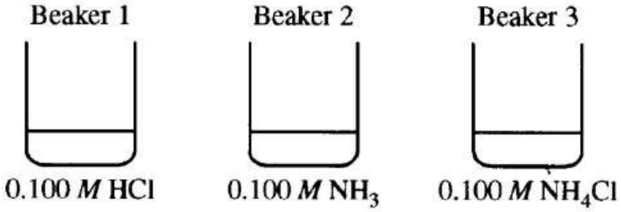
A sample of MCO_3 is placed in a previously evacuated container, heated to 423 K, and allowed to come to equilibrium. Some solid MCO_3 remains in the container. The value of K_P for the reaction at 423 K is 0.0012.

i. Write the equilibrium constant expression for K_P of the reaction.

ii. Determine the pressure, in atm, of $CO_2(g)$ in the container at equilibrium at 423 K.

iii. Indicate whether the value of ΔG^o for the reaction at 423 K is positive, negative, or zero. Justify your answer.

2011 Q1



1. Each of three beakers contains 25.0 mL of a 0.100 M solution of HCl, NH_3, or NH_4Cl, as shown above. Each solution is at 25 °C.

a. Determine the pH of the solution in beaker 1. Justify your answer.

b. In beaker 2, the reaction $NH_3(aq) + H_2O(l)$ ⓧ $NH_4^+(aq) + OH^-(aq)$ occurs. The value of K_b for $NH_3(aq)$ is 1.8×10^{-5} at 25 °C.

i. Write the K_b expression for the reaction of $NH_3(aq)$ with $H_2O(l)$.

ii. Calculate the $[OH^-]$ in the solution in beaker 2.

c. In beaker 3, the reaction $NH_4^+(aq) + H_2O(l)$ ⓧ $NH_3(aq) + H_3O^+(aq)$ occurs.

i. Calculate the value of K_a for NH_4^+ at 25 °C.

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.

d. The contents of beaker 1 are poured into the solution made in part c) ii). The resulting solution is stirred. Assume that volumes are additive.

i. Is the resulting solution an effective buffer? Justify your answer.

ii. Calculate the final $[NH_4^+]$ in the resulting solution at 25 °C.

2012 Q1

1. A 1.22 g sample of a pure monoprotic acid, HA, was dissolved in distilled water. The HA solution was then titrated with 0.250 M NaOH. The pH was measured throughout the titration, and the equivalence point was reached when 40.0 mL of the NaOH solution had been added. The data from the titration are recorded in the table below.

Volume of 0.250 M NaOH Added (mL)	pH of titrated Solution
0.00	?
10.0	3.72
20.0	4.20
30.0	?
40.0	8.62
50.0	12.40

a. Explain how the data in the table above provide evidence that HA is a weak acid rather than a strong acid.

b. Write the balanced net-ionic equation for the reaction that occurs when the solution of NaOH is added to the solution of HA.

c. Calculate the number of moles of HA that were titrated.

d. Calculate the molar mass of HA.

The equation for the dissociation reaction of HA in water is shown below.

$HA(aq) + H_2O(l) \otimes H_3O^+(aq) + A^-(aq)$ $K_a = 6.3 \times 10^{-5}$

e. Assume that the initial concentration of the HA solution (before any NaOH solution was added) is 0.200 M. Determine the pH of the initial HA solution.

f. Calculate the value of $[H_3O^+]$ in the solution after 30.0 mL of NaOH is added and the total volume of the solution is 80.0 mL

2012B Q1

1. $CH_3NH_2(aq) + H_2O(l) \otimes CH_3NH_3^+(aq) + OH^-(aq)$ $K_b = 4.4 \times 10^{-4}$

Methylamine, CH_3NH_2, is a weak base that reacts with water according to the equation above. A student obtains a 50.0 mL sample of a methylamine solution and determines the pH of the solution to be 11.77

a. Write the expression of the equilibrium constant, K_b, for methylamine.

b. Calculate the molar concentration of OH^- in the 50.0 mL sample of the methylamine solution.

c. Calculate the initial molar concentration of $CH_3NH_2(aq)$ in the solution before it reacted with water and equilibrium was established.

The 50.0 mL sample of the methylamine solution is titrated with an HCl solution of unknown concentration. The equivalence point of the titration is reached after a volume of 36.0 mL of the HCl solution is added. The pH of the solution at the equivalence point is 5.98.

d. Write the net-ionic equation that represents the reaction that takes place during the titration.

e. Calculate the concentration of the HCl solution used to titrate the methylamine.

f. Using the axes provided, sketch the titration curve that results from the titration described above. On the graph, clearly label the equivalence point of the titration.

Multiple Choice Questions

2013

26. For which of the following reaction mixtures at equilibrium would reducing the volume of the container at constant temperature cause the equilibrium to shift toward the products?

a. $SrCO_3(s)$ ⓧ $SrO(s) + CO_2(g)$

b. $C(s) + CO_2(g)$ ⓧ $2\ CO(g)$

c. $CO(g) + H_2O(g)$ ⓧ $CO_2(g) + H_2(g)$

d. $PCl_5(g)$ ⓧ $PCl_3(g) + Cl_2(g)$

e. $2\ NO_2(g)$ ⓧ $N_2O_4(g)$

30. The equilibrium constant for the gas phase reaction above is 95 at 25 °C. What is the value of the equilibrium constant for the following reaction at 25 °C?

$O_2(g) + 4\ NO_2(g)$ ⓧ $2\ N_2O_5(g)$

a. $(95)^2$
b. 95
c. $(95)^{1/2}$
d. $1/95$
e. $1/(95)^2$

$$HSO_4^-(aq) + CO_3^{2-}(aq) \otimes SO_4^{2-}(aq) + HCO_3^-(aq)$$

40. The reaction represented above is observed to proceed spontaneously to the right in aqueous solution. In this system the strongest base is

a. $SO_4^{2-(}$*aq*)
b. $CO_3^{2-(}$*aq*)
c. H_2O(*l*)
d. HCO_3^-(*aq*)
e. HSO_4^-(*aq*)

55. Which of the following statements is true for the equilibrium vapor pressure of a liquid in a closed system?

a. It remains constant when the temperature increases.
b. It decreases to half its original value if the volume of the gas phase is doubled.
c. It increases to twice its original value if the volume of the liquid phase is doubled.
d. It decreases to half its original value if the surface area of the liquid is reduced by one-half.
e. It is independent of the volume of the vapor phase.

$$X(g) + Y(g) \otimes 2\,Z(g)$$

60. When 4.00 mol each of X(*g*) and Y(*g*) are placed in a 1.00 L vessel and allowed to react at constant temperature according to the equation above, 6.00 mol of Z(*g*) is produced. What is the value of the equilibrium constant, K_c ?
a. 3
b. 6
c. 8
d. 16
e. 36

2013 AB

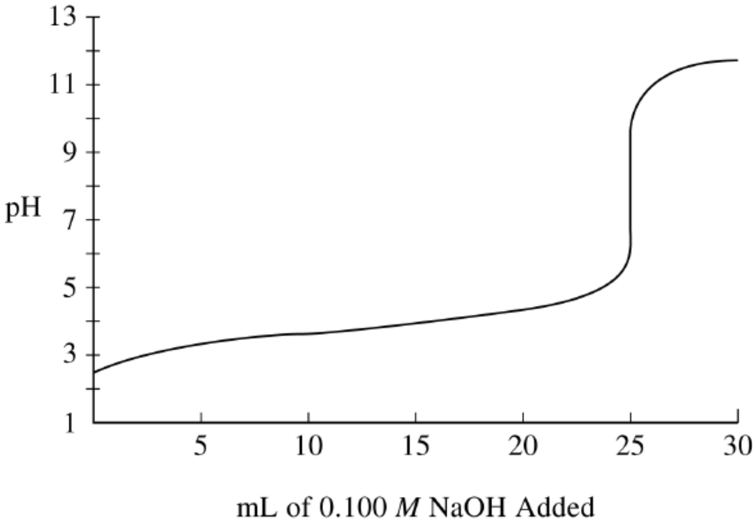
$$HSO_4^-(aq) + CO_3^{2-}(aq) \otimes SO_4^{2-}(aq) + HCO_3^-(aq)$$

40. The reaction represented above is observed to proceed spontaneously to the right in aqueous solution. In this system the strongest base is

a. SO_4^{2-}(aq)
b. CO_3^{2-}(aq)
c. H_2O(*l*)
d. HCO_3^-(aq)
e. HSO_4^-(aq)

45. A 0.10 *M* solution of a weak monoprotic acid has a pH equal to 4.0. The ionization constant, K_a, of the acid is

a. 1×10^{-3}
b. 1×10^{-4}
c. 1×10^{-7}
d. 1×10^{-8}
e. 1×10^{-9}



56. An unknown acid is dissolved in 25 mL of water and titrated with 0.100 *M* NaOH. The results are shown in the titration curve above. Which of the following could be the unknown acid?

a. Fluoroacetic acid, $pK_a = 2.6$
b. Glycolic acid, $pK_a = 3.8$
c. Propanoic acid, $pK_a = 4.9$
d. Hypochlorous acid, $pK_a = 7.5$
e. Boric acid, $pK_a = 9.3$

Laboratory

Concepts – LABORATORY QUESTIONS – contained in several Big Ideas and the Science Practices

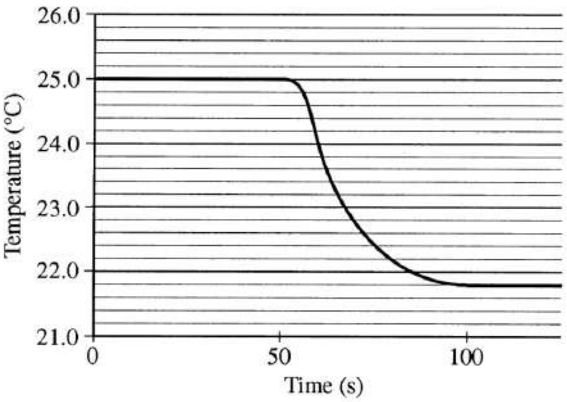
1. Vocabulary words

ppt (precipitate)

Free Response Questions

2010 Q2 Thermo Lab

2. A student performs an experiment to determine the molar enthalpy of solution of urea, H_2NCONH_2. The student places 91.95 g of water at 25 °C into a coffee-cup calorimeter and immerses a thermometer in the water. After 50 s, the student adds 5.13 g of solid urea, also at 25 °C, to the water and measures the temperature of the solution as the urea dissolves. A plot of the temperature data is shown in the graph below.



a. Determine the change in temperature of the solution that results from the dissolution of the urea.

b. According to the data, is the dissolution of urea in water an endothermic process or an exothermic process? Justify your answer.

c. Assume that the specific heat capacity of the calorimeter is negligible and that the specific heat capacity of the solution of urea and water is 4.2 J g^{-1} $^{\circ}C^{-1}$ throughout the experiment.

i. Calculate the heat of dissolution of the urea in joules.

ii. Calculate the molar enthalpy of solution, ΔH_{soln}°, of urea in kJ mol^{-1}.

d. Using the information in the table below, calculate the value of the molar entropy of solution, ΔS_{soln}^{o}, of urea at 298 K. Include units with your answer.

	Accepted value
ΔH_{soln}^{o} of urea	14.0 kJ mol^{-1}
ΔG_{soln}^{o} of urea	-6.9 kJ mol^{-1}

e. The student repeats the experiment and this time obtains a result for ΔH_{soln}^{o} of urea that is 11 percent below the accepted value. Calculate the value of ΔH_{soln}^{o} that the student obtained in this second trial.

f. The student performs a third trial of the experiment but this time adds urea that has been taken directly from a refrigerator at 5 ^{o}C. What effect, in any, would using the cold urea instead of urea at 25 ^{o}C have on the experimentally obtained value of ΔH_{soln}^{o}? Justify your answer.

2011B #5

5. A student is instructed to prepare 100.0 mL of 1.250 M NaOH from a stock solution of 5.000 M NaOH. The student follows the proper safety guidelines.

a. Calculate the volume of 5.000 M NaOH needed to accurately prepare 100.0 mL of 1.250 M NaOH.

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

Balance
50 mL buret
Eyedropper
25 mL Erlenmeyer flask
100 mL Florence flask
Drying oven
100 mL graduated cylinder
25 mL pipet
Wash bottle of distilled H_2O
100 mL volumetric flask
100 mL beaker
Crucible

c. The student is given 50.0 mL of a 1.00 M solution of a weak, monoprotic acid, HA. The solution is titrated with the 1.250 M NaOH to the endpoint. (Assume that the endpoint is at the equivalence point.)

i. Explain why the solution is basic at the equivalence point of the titration. Include a chemical equation as part of your explanation.

ii. Identify the indicator in the table below that would be best for the titration. Justify your choice.

Indicator	pKa
Methyl Red	5

Bromothymol blue	7
Phenolphthalein	9

d. The student is given another 50.0 mL sample of 1.00 M HA, which the student adds to the solution that had been titrated to the endpoint in part c). The result is a solution with a pH of 5.0.

i. What is the value of the acid dissociation constant, K_a, for the weak acid? Explain your reasoning.

ii. Explain why the addition of a few drops of 1.250 M NaOH to the resulting solution does not appreciably change its pH.

2012 B Q6

6. In a laboratory experiment, Pb and an unknown metal Q were immersed in solutions containing aqueous ions of unknown metals Q and X. The following reactions summarize the observations.

Observation 1: $Pb(s) + X^{2+}(aq) \rightarrow Pb^{2+}(aq) + X(s)$

Observation 2: $Q(s) + X^{2+}(aq) \rightarrow$ no reaction

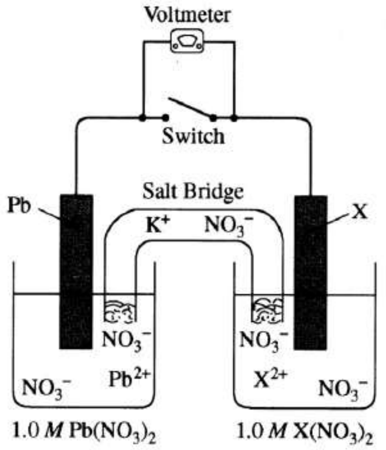
Observation 3: $Pb(s) + Q^{2+}(aq) \rightarrow Pb^{2+}(aq) + Q(s)$

a. On the basis of the reactions indicated above, arrange the three metals, Pb, Q, and X, in order from least reactive to the most reactive on the lines provided below.

___________ , _______________, _______________

Least reactive metal Most reactive metal

The diagram below shows an electrochemical cell that is constructed with a Pb electrode immersed in 100. mL of 1.0 M $Pb(NO_3)_2(aq)$ and an electrode made of metal X immersed in 100. mL of 1.0 M $X(NO_3)_2(aq)$. A salt bridge containing saturated aqueous KNO_3 connects the anode compartment to the cathode compartment. The electrodes are connected to an external circuit containing a switch, which is open. When a voltmeter is connected to the circuit as shown, the reading on the voltmeter is 0.47 V. When the switch is closed, electrons flow through the switch from the Pb electrode toward the X electrode.



b. Write the equation for the half reaction that occurs at the anode.

c. The value of the standard potential for the cell, *E*°, is 0.47 V.

   i. Determine the standard reduction potential for the half reaction that occurs at the cathode.

   ii. Determine the identity of metal X.

d. Describe what happens to the mass of each electrode as the cell operates.

2011 A Q2

2. A student is assigned the task of determining the mass percent of silver in an alloy of copper and silver by dissolving a sample of the alloy in excess nitric acid and then precipitating the silver as AgCl.

First the student prepares 50. mL of 6 M HNO_3.

a. The student is provided with a stock solution of 16 M HNO_3, two 100 mL graduated cylinders that can be read to ± 1 mL, a 100 mL beaker that can be read to ± 10 mL, safety goggles, rubber gloves, a glass stirring rod, a dropper, and distilled H_2O.

   i. Calculate the volume, in mL, of 16 M HNO_3 that the student should use for preparing 50. mL of 6 M HNO_3.

   ii. Briefly list the steps of an appropriate and safe procedure for preparing the 50. mL of 6 M HNO_3. Only materials selected from those provided to the student (listed above) may be used.

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

iv. During the preparation of the solution, the student accidently spills about 1 mL of 16 M HNO_3 on the bench top. The student finds three bottles containing liquids sitting near the spill: a bottle of distilled water, a bottle of 5 percent $NaHCO_3(aq)$, and a bottle of saturated NaCl(aq). Which of the liquids is best to use in cleaning up the spill? Justify your choice.

Then the student pours 25 mL of the 6 M HNO_3 into a beaker and adds a 0.6489 g sample of the alloy. After the sample completely reacts with the acid, some saturated NaCl(aq) is added to the beaker, resulting in the formation of an AgCl precipitate. Additional NaCl(aq) is added until no more precipitate is observed to form. The precipitate is filtered, dried, and weighed to constant mass in a filter crucible. The data are shown in the table below.

Mass of sample of copper - silver alloy	0.6489 g
Mass of dry filter crucible	28.7210 g
Mass of filter crucible and precipitate (1st weighing)	29.3587 g
Mass of filter crucible and precipitate (2nd weighing)	29.2599 g
Mass of filter crucible and precipitate (3rd weighing)	29.2598 g

b. Calculate the number of moles of AgCl precipitate collected.

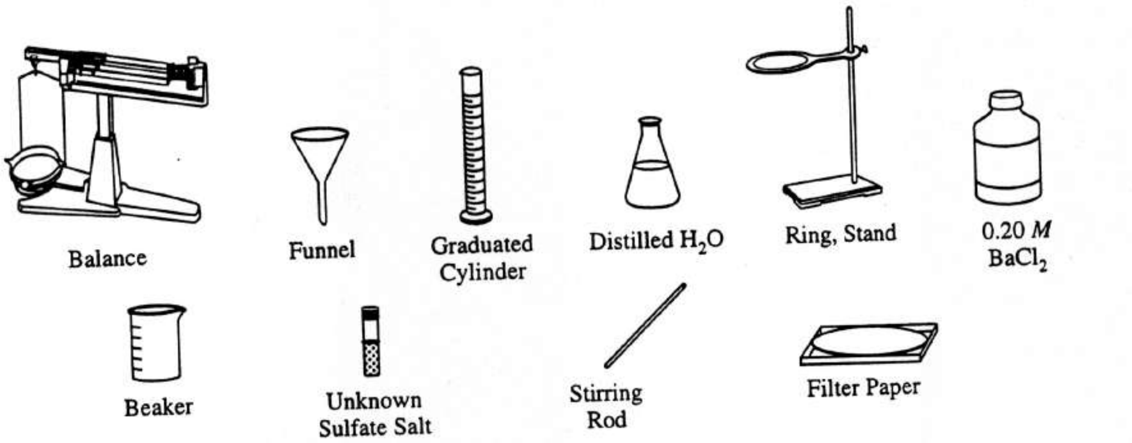
c. Calculate the mass percent of silver in the alloy of copper and silver.

1992 Q 7

7. Four bottles, each containing about 5 grams of finely powdered white substance, are found in a laboratory. Near the bottles are four labels specifying high purity and indicating that the substances are glucose ($C_6H_{12}O_6$), sodium chloride (NaCl), aluminum oxide (Al_2O_3), and zinc sulfate ($ZnSO_4$).

Assume that these labels belong to the bottles and that each bottle contains a single substance. Describe the tests you would conduct to determine which label belongs to which bottle. Give the results you would expect for each test.

1997 #9



An experiment is to be performed to determine the mass percent of sulfate in an unknown soluble sulfate salt. The equipment shown above is available for the experiment. A drying oven is also available.

a. Briefly list the steps needed to carry out this experiment.

b. What experimental data need to be collected to calculate the mass percent of sulfate in the unknown?

c. List the calculations necessary to determine the mass percent of sulfate in the unknowm.

d. Would 0.20 M $MgCl_2$ be an acceptable substitute for the $BaCl_2$ solution provided for this experiment? Explain.

Multiple Choice

2013

33. For an experiment, a student needs 100.0 mL of 0.4220 *M* NaCl. If the student starts with NaCl(*s*) and distilled water, which of the following pieces of laboratory glassware should the student use to prepare the solution with the greatest accuracy?

    a. 25 mL volumetric pipet
    b. 100 mL Erlenmeyer flask
    c. 100 mL graduated cylinder
    d. 100 mL volumetric flask
    e. 1 L beaker

38. The percentage of silver in a solid sample is determined gravimetrically by converting the silver to Ag^+(*aq*) and precipitating it as silver chloride. Failure to do which of the following could cause errors in the analysis?

    I. Account for the mass of the weighing paper when determining the mass of the sample
    II. Measure the temperature during the precipitation reaction

III. Wash the precipitate
IV. Heat the AgCl precipitate to constant mass

a. I only
b. I and II
c. I and IV
d. II and III
e. I, III, and IV

48. Potassium hydrogen phthalate, KHP, is used as a primary standard for determining the concentration of a solution of NaOH by titration. If the KHP has not been dried before weighing, the calculated molarity of the NaOH would be

a. higher than the actual value, since water is included in the apparent mass of KHP

b. higher than the actual value, since the presence of water requires a larger volume of titrant

c. lower than the actual value, since NaOH absorbs water

d. unaffected, since KHP is a strong acid

e. unaffected, since water is routinely added before the titration

$$NaOH(aq) + HCl(aq) \rightarrow H_2O(l) + NaCl(aq)$$

65. A student is trying to determine the heat of reaction for the acid-base neutralization reaction represented above. The student uses 0.50 *M* NaOH and 0.50 *M* HCl solutions. Which of the following situations, by itself, would most likely result in the LEAST error in the calculated value of the heat of reaction?

a. The thermometer was incorrectly calibrated and read 0.5 Celsius degree too high during the procedure.

b. The volume of the acid solution added to the calorimeter was actually 1.0 mL less than what was recorded.

c. The calorimeter was poorly insulated, and some heat escaped to the atmosphere during the procedure.

d. The actual molarity of the base solution was 0.53 *M* but was recorded as 0.50 *M*.

e. The final temperature of the mixture was taken before the contents of the calorimeter had reached thermal equilibrium.