UNITS TO COVER

Bonding

1. Forces
   1. Types: ionic, covalent, metallic, hydrogen bonding, van der waals (including London dispersion forces)
   2. Relationships to states, structure, and properties of matter
   3. Polarity, electronegativity
2. Molecular models
   1. Lewis structures
   2. Valence electrons, hybridization of orbitals, resonance (leads to fractional bond orders), sigma and pi bonds
   3. VSEPR
3. Geometry of molecules and ions, structure isomerism of simple organic molecules and coordination complexes, dipole moments, relation of properties to structure

Equilibrium

1. Dynamic equilibrium, physical and chemical; Le Chatelier’s law; equilibrium constants
   1. Two basic problem types
      1. K 🡪 [ ]
      2. [ ] 🡪 K
   2. Solid/liquid? Use stoich and the CHANGE line
2. Quantitative treatment
   1. Equilibrium constants for gaseous reactions: Kp, Kc
   2. Equilibrium constants for reaction in solution
      1. Constants for acids and bases, pK, pH
      2. Solubility product constants and their application to precipitation and dissolution of slightly soluble compounds, Ksp
      3. Common ion effect, buffers, hydrolysis

Solutions

1. Types of solutions and factors affecting solubility of solids and solubility of gases
2. Molarity, molality, mole fraction, density, percent by mass
3. colligative properties
4. Ksp (super important)
5. Normal boiling point

Acids&Bases

Acid-base, Arrhenius, bronsted-lowry, and lewis theories; coordination complexes; amphoterism

Kinetics

1. Reaction rate
2. Use of rate laws to determine order of reaction and rate constant from experimental data
3. Effect of temperature change on rates
4. Activation energy, catalysts
5. Reaction mechanisms and rate determining steps

Thermodynamics

1. First law: enthalpy change; heat of formation; hear of reaction; Hess’ law; heats of vaporization and fusion; calorimetry
2. Second law: entropy; free energy of formation; free energy of reaction; dependence of change in free energy on enthalpy and entropy changes
3. Relationship of change in free energy to equilibrium constants and electrode potentials

Nuclear

1. Atomic mass, mass number, isotope
2. Nuclear equations, half-lives, and radioactivity; chemical applications

Lab

1. Lab skills
2. Making observations, recording data, calculating and interpreting results based on data, lab safety, experimental errors

Organic – basic naming, reactions, isomerism of simple organic molecules, structure, nomenclature, chemical properties

Chemical Reactions - Chemical reactivity and products of chemical reaction

Significant figures/Mental Math

Mixtures - just stoich/reaction problems in disguise

Gas Laws – simple calculations, root-mean-square speed, nonideal behavior

Electrochemistry – not on the review, but you should remember it since we just did it!!!

**Bonding**

Questions 1 & 2 refer to the material given below. The answer to each question is one of these five lettered equations. Select the one letter whose equation is most clearly related to the question. A letter can be used more than once.

a. Br2(*l*) → Br2(*g*)

b. Br2(*g*) → 2Br(*g*)

c. Br(*g*) + e → Br–(*g*)

d. KBr(*s*) → K+(*g*) + Br–(*g*)

e. K(*s*) + 1/2 Br2(*l*) → KBr(*s*)

1. Which process represents the crystal lattice energy?

2. The process corresponding to the electron affinity is

3. Which of the following species has the shortest bond distance?

a. CO

b. NO–

c. O2

d. F2

e. Cl2

4 Which of the following species has a Lewis structure similar to H3O+?

a. NH3

b. HCO3–

c. CO32–

d. ClF3

e. NF3

5. All the following species are isoelectronic **EXCEPT**

a. Ca2+ b. Mg2+ c. Cl– d. Ar e. S2–

6. The larger the difference in electronegativity,

1. the more ionic the bond.

2. the more covalent the bond.

3. the more polar the bond.

a. 1 only b. 2 only c. 3 only d.1 and 3 only e.2 and 3 only

7 Which atom would be expected to be the most electronegative?

a. B b. Na c. N d. Cs e.Al

8. In which of the following species is there the greatest unequal sharing of the bonding electrons?

a. SO3 b. SO32– c. NH4+ d. H2O e. H2S

1973 D

Discuss briefly the relationship between the dipole moment of a molecule and the polar character of the bonds within it. With this as the basis, account for the difference between the dipole moments of CH2F2 and CF4.

1982 D

(a) Draw the Lewis electrondot structures for CO32‑, CO2, and CO, including resonance structures where appropriate.

(b) Which of the three species has the shortest C‑O bond length? Explain the reason for your answer.

(c) Predict the molecular shapes for the three species. Explain how you arrived at your predictions.

1992 D

Explain each of the following in terms of atomic and molecular structures and/or intermolecular forces.

(a) Solid K conducts an electric current, whereas solid KNO3 does not.

(b) SbCl3 has measurable dipole moment, whereas SbCl5 does not.

(c) The normal boiling point of CCl4 is 77C, whereas that of CBr4 is 190C.

(d) NaI(s) is very soluble in water, whereas I2(s) has a solubility of only 0.03 gram per 100 grams of water.

**Equilibrium**

1. If the equilibrium constant for A + B 🡨🡪C is 0.180, then the equilibrium constant for 2C 🡨🡪2A + 2B is

a) 0.640 b) 5.56 c) 0.360 d) 30.9 e) 0.180

2. Apply the law of mass action to determine the equilibrium expression for 2NO2Cl(*aq*) 🡨🡪2NO2(*aq*) + Cl2(*aq*).

a) *K* = 2[NO2][Cl2]/2[NO2Cl]

b) *K* = 2[NO2Cl]/2[NO2][Cl2]

c) *K* = [NO2Cl]2/[NO2]2[Cl2]

d) *K* = [NO2]2[Cl2]/[NO2Cl]2

e) *K* = [NO2Cl]2[NO2]2[Cl2]

3. Consider the reaction A(*g*) + B(*g*) 🡨🡪C(*g*) + D(*g*). You have the gases A, B, C, and D at equilibrium. Upon adding gas A, the value of *K*:

a) increases, because by adding A more products are made, increasing the product to reactant ratio

b) decreases, because A is a reactant so the product to reactant ratio decreases

c) does not change, because A does not figure into the product to reactant ratio

d) does not change, as long as the temperature is constant

e) depends on whether the reaction is endothermic or exothermic

4. Consider the following system at equilibrium:

N2(*g*) + 3H2(*g*) 🡨🡪2NH3(*g*) + 92.94 kJ

Which of the following changes will shift the equilibrium to the right?

I. increasing the temperature

II. decreasing the temperature

III. increasing the volume

IV. decreasing the volume

V. removing some NH3

VI. adding some NH3

VII. removing some N2

VIII. adding some N2

a) I, IV, VI, VII

b) II, III, V, VIII

answer choices continue…

c) I, VI, VIII

d) I, III, V, VII

e) II, IV, V, VIII

**1977 D**

For the system 2 SO2*(g)* + O2*(g)* ↔ 2 SO3*(g)* , Δ*H* is negative for the production of SO3. Assume that one has an equilibrium mixture of these substances. Predict the effect of each of the following changes on the value of the equilibrium constant and on the number of moles of SO3 present in the mixture at equilibrium. Briefly account for each of your predictions. (Assume that in each case all other factors remain constant.)

(a) Decreasing the volume of the system.

(b) Adding oxygen to the equilibrium mixture.

(c) Raising the temperature of the system.

**1995 A**

CO2*(g)* + H2*(g)* ↔ H2O*(g)* + CO*(g)*

When H2*(g)* is mixed with CO2*(g)* at 2,000 K, equilibrium is achieved according to the equation above. In one experiment, the following equilibrium concentrations were measured.

[H2] = 0.20 mol/L

[CO2] = 0.30 mol/L

[H2O] = [CO] = 0.55 mol/L

(a) What is the mole fraction of CO*(g)* in the equilibrium mixture?

(b) Using the equilibrium concentrations given above, calculate the value of *Kc*, the equilibrium constant for the reaction.

(c) Determine *Kp* in terms of *Kc* for this system.

(d) When the system is cooled from 2,000 K to a lower temperature, 30.0 percent of the CO*(g)* is converted back to CO2*(g)*. Calculate the value of *Kc* at this lower temperature.

(e) In a different experiment, 0.50 mole of H2*(g)* is mixed with 0.50 mole of CO2*(g)* in a 3.0-liter reaction vessel at 2,000 K. Calculate the equilibrium concentration, in moles per liter, of CO*(g)* at this temperature.

**Solutions**

1. Given that a solution is 5 percent sucrose by mass, what additional information is necessary to calculate the molarity of the solution?

I. The density of water  
II. The density of the solution  
III. The molar mass of sucrose

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

2. Which of the following solutions has the lowest freezing point?

(A) 0.20 *m* C6H12O6, glucose  
(B) 0.20 *m* NH4Br  
(C) 0.20 *m* ZnSO4  
(D) 0.20 *m* KMnO4  
(E) 0.20 *m* MgCl2

3. [You’ve seen this question before, but try working it WITHOUT A CALCULATOR]The solubility of CuI is 2 x 10¯6 molar. What is the solubility product constant, Ksp, for CuI?

(A) 1.4 x 10¯3  
(B) 2 x 10¯6  
(C) 4 x 10¯12  
(D) 2 x 10¯12  
(E) 8 x 10¯18

*::***1975 D**

Alcohol dissolves in water to give a solution that boils at a lower temperature than pure water. Salt dissolves in water to give a solution that boils at a higher temperature than pure water. Explain these facts from the standpoint of vapor pressure.

**1976 B**

(a) Calculate the molality of a 20.0 percent by weight aqueous solution of NH4Cl. (Molecular weight: NH4Cl = 53.5)

(b) If this NH4Cl solution is assumed to be ideal and is completely dissociated into ions, calculate the pressure of this solution at 29.0.

(c) Actually, a solution of NH4Cl of this concentration is not ideal. Calculate the apparent degree of dissociation of the NH4Cl if the freezing point of this solution is -15.3C? (Molal freezing point constant = 1.86C)

**1990 A**

The solubility of iron(II) hydroxide, Fe(OH)2, is 1.43x10-3 gram per litre at 25°C.

(a) Write a balanced equation for the solubility equilibrium.

(b) Write the expression for the solubility product constant, Ksp, and calculate its value.

I Calculate the pH of a saturated solution of Fe(OH)2 at 25C.

(d) A 50.0 millilitre sample of 3.00x10-3 molar FeSO4 solution is added to 50.0 millilitres of 4.00x10-6 molar NaOH solution. Does a precipitate of Fe(OH)2 form? Explain and show calculations to support your answer.

**1995 D**

Lead iodide is a dense, golden yellow, slightly soluble solid. At 25°C, lead iodide dissolves in water forming a system represented by the following equation.

PbI2*(s)* 🡨🡪 Pb2+ + 2 I- Δ*H* = +46.5 kilojoules

(a) How does the entropy of the system PbI2*(s)* + H2O*(l)* change as PbI2*(s)* dissolves in water at 25°C? Explain

(b) If the temperature of the system were lowered from 25°C to 15°C, what would be the effect on the value of *Ksp*? Explain.

I If additional solid PbI2 were added to the system at equilibrium, what would be the effect on the concentration of I- in the solution? Explain.

(d) At equilibrium, Δ*G* = 0. What is the initial effect on the value of *G* of adding a small amount of Pb(NO3)2 to the system at equilibrium? Explain.

**Acids&Bases DON’T USE A CALCULATOR**

Given the following acids and *K*a values:

HclO4 HOAc HCN HF

1 × 107 1.76 × 10–5 4.93 × 10–10 3.53 × 10–4

What is the order of increasing base strength?

a) CN–, F–, Oac–, ClO4–

b) CN–, Oac–, F–, ClO4–

c) CN–, ClO4–, F–, Oac–

d) ClO4–, Oac–, CN–, F–

e) ClO4–, F–, Oac–, CN–

2. A 50.00-mL solution of 0.0350 *M* nitrous acid (*K*a = 4.0 × 10–4) is titrated with a 0.0215 *M* solution of sodium hydroxide as the titrant. What is the pH of the acid solution after 15.00 mL of titrant have been added?

a) 1.46 b) 2.45 c) 2.88 d) 10.16 e) 3.40

3. A 100.0-mL sample of 0.503 *M* H2A (diprotic acid) is titrated with 0.200 *M* NaOH. After 125.0 mL of 0.200 *M* NaOH has been added, the pH of the solution is 4.50. Calculate Ka1 for H2A.

a) 3.2 × 10–10

b) 4.5

c) 3.1 × 10–5

d) not enough information to calculate

e) none of these

4. What quantity of NaOH(*s*) must be added to 2.00 L of 0.538 *M* HCl to achieve a pH of 13.00? (Assume no volume change.)

a) 0.88 mol

b) 1.28 mol

c) 0.20 mol

d) 1.00 × 10–13 mol

e) none of these

5. Which of the following ions is the strongest Lewis acid?

(A) Na+

(B) Cl¯

(C) CH3COO¯

(D) Mg2+

(E) Al3+

1989 A

In an experiment to determine the molecular weight and the ionization constant for ascorbic acid (vitamin C), a student dissolved 1.3717 grams of the acid in water to make 50.00 millilitres of solution. The entire solution was titrated with a 0.2211 molar NaOH solution. The pH was monitored throughout the titration. The equivalence point was reached when 35.23 millilitres of the base has been added. Under the conditions of this experiment, ascorbic acid acts as a monoprotic acid that can be represented as HA.

(a) From the information above, calculate the molecular weight of ascorbic acid.

(b) When 20.00 millilitres of NaOH had been added during the titration, the pH of the solution was 4.23. Calculate the acid ionization constant for ascorbic acid.

I Calculate the equilibrium constant for the reaction of the ascorbate ion, A-, with water.

(d) Calculate the pH of the solution at the equivalence point of the titration.

**1992 D**

The equations and constants for the dissociation of three different acids are given below.

HCO3- ⬄ H+ + CO32- Ka = 4.2 x 10-7

H2PO4- ⬄ H+ + HPO42- Ka = 6.2 x 10-8

HSO4- <=> H+ + SO42- Ka = 1.3 x 10-2

(a) From the systems above, identify the conjugate pair that is best for preparing a buffer with a pH of 7.2. Explain your choice.

(b) Explain briefly how you would prepare the buffer solution described in (a) with the conjugate pair you have chosen.

(c) If the concentrations of both the acid and the conjugate base you have chosen were doubled, how would the pH be affected? Explain how the capacity of the buffer is affected by this change in concentrations of acid and base.

(d) Explain briefly how you could prepare the buffer solution in (a) if you had available the solid salt of the only one member of the conjugate pair and solution of a strong acid and a strong base.

**Kinetics**

1. The rate constant for a reaction is 1.6 × 10–2 s–1 at 680 K and 4.6 × 10–2 s–1 at 890 K. What is the activation energy?

a) 11 kJ/mol b) 25 kJ/mol c) 660 kJ/mol d) 3000 kJ/mol

e) This can't be solved without knowing the frequency factor.

2. The reaction 2NO + O2 → 2NO2 obeys the rate law –Δ [O2] = *k* [NO]2[O2].

Δ t

Which of the following mechanisms is consistent with the experimental rate law?

(a) NO + NO → N2O2 (slow) (c)2NO N2O2 (fast equilibrium)

N2O2 + O2 → 2NO2 (fast) N2O2 → NO2 + O (slow)

6NO + O → NO2 (fast)

(b) NO + O2 NO3 (fast equilibrium)

NO3 + NO → 2NO2 (slow) (d)O2 + O2 → O2 + O2 (slow)

O2 + NO → NO2 + O (fast)

(e) none of these O + NO → NO2 (fast)

1980 D

The decomposition of compound X is an elementary process that proceeds as follows: kf

X(g)<===> A(g)+ B(g)

kr ΔH° for the above reaction = +15 kilocalories

The forward reaction is slow at room temperature but becomes rapid when a catalyst is added.

(a) Draw a diagram of potential energy *vs* reaction coordinate for the uncatalyzed reaction. On this diagram label:

(1) the axes

(2) the energies of the reactants and the products

(3) the energy of the activated complex

(4) all significant energy differences

(b) On the same diagram indicate the change or changes that result from the addition of the catalyst. Explain the role of the catalyst in changing the rate of the reaction.

(c) If the temperature is increased, will the ratio kf/kr increase, remain the same, or decrease? Justify your answer with a one or two sentence explanation. [kf and kr are the specific rate constants for the forward and the reverse reactions, respectively.]

1983 C Graphical methods are frequently used to analyze data and obtain desired quantities.

(a) 2 HI*(g)* --> H2*(g)* + I2*(g)*

The following data give the value of the rate constant at various temperatures for the gas phase reaction above.

|  |  |
| --- | --- |
| T (K) | *k* (litre/mol sec) |
| 647 | 8.58 x 10B5 |
| 666 | 2.19 x 10B4 |
| 683 | 5.11 x 10B4 |
| 700 | 1.17 x 10B3 |
| 716 | 2.50 x 10B3 |

Describe, without doing any calculations, how a graphical method can be used to obtain the activation energy for this reaction.

(b) A*(g)* -> B*(g)* + C*(g)* The following data give the partial pressure of A as a function of time and were obtained at 100C for the reaction above.

|  |  |
| --- | --- |
| PA (mm Hg) | t (sec) |
| 348 | 0 |
| 247 | 600 |
| 185 | 1200 |
| 105 | 2400 |
| 58 | 3600 |

Describe, without doing any calculations, how graphs can be used to determine whether this reaction is first or second order in A and how these graphs are used to determine the rate constant.

1994 B 2 NO*(g)* +2 H2*(g)* -> N2*(g)* + 2 H2O*(g)*

Experiments were conducted to study the rate of the reaction represented by the equation above. Initial concentrations and rates of reaction are given in the table below.

|  |  |  |  |
| --- | --- | --- | --- |
|  | Initial Concentration (mol/L) | | Initial Rate of Formation of N2 |
| Exp | [NO] | [H2] | (mol/L**.**min) |
| 1 | 0.0060 | 0.0010 | 1.8 x 10B4 |
| 2 | 0.0060 | 0.0020 | 3.6 x 10B4 |
| 3 | 0.0010 | 0.0060 | 0.30 x 10B4 |
| 4 | 0.0020 | 0.0060 | 1.2 x 10B4 |

(a) (i) Determine the order for each of the reactants, NO and H2, from the data given and show your reasoning.

(ii) Write the overall rate law for the reaction.

(b) Calculate the value of the rate constant, *k*, for the reaction. Include units.

(c) For experiment 2, calculate the concentration of NO remaining when exactly one‑half of the original amount of H2 had been consumed.

(d) The following sequence of elementary steps is a proposed mechanism for the reaction.

I. NO + NO -> N2O2

II. N2O2 + H2->H2O + N2O

III. N2O + H2 -> N2 + H2O

Based on the data presented, which of the above is the rate‑determining step? Show that the mechanism is consistent with

(i) the observed rate law for the reaction, and

(ii) the overall stoichiometry of the reaction.

**Thermodynamics**

Most important equation: ∆G=∆H-T∆S (units must match!!!)

Questions 1-4 refer to the following types of energy.

(A) Activation energy  
(B) Free energy  
(C) Ionization energy  
(D) Kinetic energy  
(E) Lattice energy

1. The energy required to convert a ground-state atom in the gas phase to a gaseous positive ion

2. The energy change that occurs in the conversion of an ionic solid to widely separated gaseous ions

3. The energy in a chemical or physical change that is available to do useful work

4. The energy required to form the transition state in a chemical reaction

5. I2(g) + 3 Cl2(g) ---> 2 ICl3(g)

According to the data in the table below, what is the value of H° for the reaction represented above?

|  |  |
| --- | --- |
| Bond | Average Bond Energy (kilojoules / mole) |
| I---I | 149 |
| Cl---Cl | 239 |
| I---Cl | 208 |

(A) - 860 kJ (D) + 450 kJ  
(B) - 382 kJ (E) + 1,248 kJ  
(C) + 180 kJ  
  
6. CH4(g) + 2 O2(g) ---> CO2(g) + 2 H2O(l);  = - 889.1 kJ

Hf° H2O(l) = - 285.8 kJ / mole

Hf° CO2(g) = - 393.3 kJ / mole

What is the standard heat of formation of methane, Hf° CH4(g), as calculated from the data above?

(A) -210.0 kJ/mole  
(B) -107.5 kJ/mole  
(C) -75.8 kJ/mole  
(D) 75.8 kJ/mole  
(E) 210.0 kJ/mole

7. Which of the following is probably true for a solid solute with a highly endothermic heat of solution when dissolved in water?

(A) The solid has a low lattice energy.  
(B) As the solute dissolves, the temperature of the solution increases.  
(C) The resulting solution is ideal.  
(D) The solid is more soluble at higher temperatures.  
(E) the solid has a high energy of hydration.

**1972**

Br2 + 2 Fe2+*(aq)* 🡪2 Br-*(aq)* + 2 Fe3+*(aq)*

For the reaction above, the following data are available:

2 Br-*(aq)* 🡪 Br2*(l)* + 2e- E° = -1.07 volts

Fe2+*(aq)* 🡪Fe3+*(aq)* + e- E° = -0.77 volts

S°, cal/mole °C

Br2*(l)* 58.6 Fe2+*(aq)* -27.1

Br-*(aq)* 19.6 Fe3+*(aq)* -70.1

(a) Determine Δ*S*°

(b) Determine Δ*G*°

(c) Determine Δ*H*°

**1988 D**

An experiment is to be performed to determine the standard molar enthalpy of neutralization of a strong acid by a strong base. Standard school laboratory equipment and a supply of standardized 1.00 molar HCl and standardized 1.00 molar NaOH are available.

(a) What equipment would be needed?

(b) What measurements should be taken?

(c) Without performing calculations, describe how the resulting data should be used to obtain the standard molar enthalpy of neutralization.

(d) When a class of students performed this experiment, the average of the results was -55.0 kilojoules per mole. The accepted value for the standard molar enthalpy of neutralization of a strong acid by a strong base is -57.7 kilojoules per mole. Propose two likely sources of experimental error that could account for the result obtained by the class.

**Nuclear**

Alpha – helium nucleus (2pro,2neut), big, slow, pos charged, ionizing, stopped by air, paper

Beta – electron, small, fast, neg charged, ionizing, stopped by foil, thick plastic, things decay by beta when their neutron/proton ratio is too large

Positron – positively charged beta particle

Gamma – EMR, fast, no mass, no charge, stopped by thick lead

Fusion – when two nuclei come together to form one large nucleus; requires energy because the repulsive forces between the two positively-charged nuclei have to be overcome

Fission – the splitting of a nuclei into smaller parts, often releases neutrons which carry on the chain reaction, happens easily with large unstable nuclei

**Half-lives**

* All nuclear reactions decay according to first order kinetics. This is a good thing, because the rate of decay is independent of the concentration: half a substance will decay during the amount of time known as its half-life
* You should be able to look at a table to identify the half-life or just use logic

**Mass Defect and Binding Energy**

* MAKING A NUCLEUS: the mass of the nucleus is less than the sum of its parts (‘mass defect’ = difference in masses; the extra mass is lost as energy)
* DESTROYING A NUCLEUS: you must put in some extra energy (called the ‘binding energy’) to break a nucleus down
* Use E=mc2 (energy in joules and mass in kilograms; little difference in mass makes a LOT of energy)

1. Which of the following represents a pair of isotopes?

|  |  |  |  |
| --- | --- | --- | --- |
|  |  | Atomic Number | Mass Number |
| (A) | I. II. | 6 7 | 14 14 |
| (B) | I. II. | 6 14 | 7 14 |
| (C) | I. II. | 6 14 | 14 28 |
| (D) | I. II. | 7 7 | 13 14 |
| (E) | I. II. | 8 16 | 16 20 |

2. When 84-Po-214 decays, the emission consists consecutively of an alpha particle, then two beta particles, and finally another alpha particle. The resulting stable nucleus is

(A) 83-Bi-206  
(B) 83-Bi-210  
(C) 82-Pb-206  
(D) 82-Pb-208  
(E) 81-Tl-210

3. Ca, V, Co, Zn, As

Gaseous atoms of which of the elements above are paramagnetic?

(A) Ca and As only  
(B) Zn and As only  
(C) Ca, V, and Co only  
(D) V, Co, and As only  
(E) V, Co, and Zn only

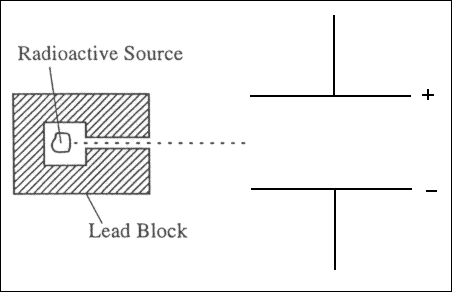
**1997**

Answer each of the following questions regarding radioactivity.

a) Write the nuclear equation for decay of 94-Pu-234 by alpha emission.

b) Account for the fact that the total mass of the products of the reaction in part (a) is slightly less than that of the original 94-Pu-234.

c) Describe how , , and  rays each behave when they pass through an electric field. Use the diagram below to illustrate your answer.



d) Why is it not possible to eliminate the hazard of nuclear waste by the process of incinertion?

**Lab**

**Read over your lab notebook!!!!**

1. The addition of an oxidizing agent such as chlorine water to a clear solution of an unknown compound results in the appearance of a brown color. When this solution is shaken with the organic solvent, methylene dichloride, the organic solvent layer turns purple. The unknown compound probably contains

(A) K+ (B) Br¯ (C) NO3¯ (D) I¯ (E) Co2+

A student prepared five 25.00-milliliter samples of hydrochloric acid and transferred each sample to an Erlenmeyer flask, diluted it with distilled water, and added a few drops of phenolphthalein to each. Each sample was then titrated with a sodium hydroxide solution to the appearance of the first permanent faint pink color. The following results were obtained.

Volumes of NaOH Solution

First Sample..................35.22 mL  
Second Sample..............36.14 mL  
Third Sample.................36.13 mL  
Fourth Sample..............36.15 mL  
Fifth Sample..................36.12 mL

Which of the following is the most probable explanation for the variation in the student’s results?

(A) The burette was not rinsed with NaOH solution.  
(B) The student misread a 5 for a 6 on the burette when the first sample was titrated.  
(C) A different amount of water was added to the first sample.  
(D) The pipette was not rinsed with the HCI solution.  
(E) The student added too little indicator to the first sample.

3. A student wishes to prepare 2.00 liters of 0.100-molar KIO3 (molecular weight 214). The proper procedure is to weigh out

(A) 42.8 grams of KIO3 and add 2.00 kilograms of H2O  
(B) 42.8 grams of KIO3 and add H2O until the final homogeneous solution has a volume of 2.00 liters  
(C) 21.4 grams of KIO3 and add H2O until the final homogeneous solution has a volume of 2.00 liters  
(D) 42.8 grams of KIO3 and add 2.00 liters of H2O  
(E) 21.4 grams fo KIO3 and add 2.00 liters of H2O

4. A compound is heated to produce a gas whose molecular weight is to be determined. The gas is collected by displacing water in a water-filled flask inverted in a trough of water. Which of the following is necessary to calculate the molecular weight of the gas, but does NOT need to be measured during the experiment?

(A) Mass of the compound used in the experiment  
(B) Temperature of the water in the trough  
(C) Vapor pressure of the water  
(D) Barometric pressure  
(E) Volume of water displaced from the flask

**1998 D**

An approximately 0.1-molar solution of NaOH is to be standardized by titration. Assume that the following materials are available.

• Clean, dry 50 mL buret

• 250 mL Erlenmeyer flask

• Wash bottle filled with distilled water

• Analytical balance

• Phenolphthalein indicator solution

• Potassium hydrogen phthalate, KHP, a pure solid monoprotic acid (to be used as the primary standard)

(a) Briefly describe the steps you would take, using the materials listed above, to standardize the NaOH solution.

(b) Describe (*i.e.*, set up) the calculations necessary to determine the concentration of the NaOH solution.

(c) After the NaOH solution has been standardized, it is used to titrate a weak monoprotic acid, HX. The equivalence point is reached when 25.0 mL of NaOH solution has been added. In the space provided at the right, sketch the titration curve, showing the pH changes that occur as the volume of NaOH solution added increases from 0 to 35.0 mL. Clearly label the equivalence point on the curve.



(d) Describe how the value of the acid-dissociation constant, *Ka,* for the weak acid HX could be determined from the titration curve in part (c).

(e) The graph below shows the results obtained by titrating a different weak acid, H2Y, with the standardized NaOH solution. Identify the negative ion that is present in the highest concentration at the point in the titration represented by the letter *A* on the curve.



**Organic**

Alkane, Alkene, Alkyne, Alcohol, Carboxylic acid, Halides, Aldehyde, Ketone, Esters

**Chemical Reactions**

Combustion, Decomp, Single (also redox), Double, Synthesis, Redox

2010 chemical reactions (balanced NIE)

1. A 0.2 M potassium hydroxide solution is titrated with a 0.1 M nitric acid solution. Q: What would be observed if the solution was titrated well past the equivalence point using bromthymol blue as the indicator? (Bromthymol blue is yellow is acidic solution and blue in basic solution.)
2. Propane is burned completely in excess oxygen gas. Q: When the products of the reaction are bubbled through distilled water, is the resulting solution neutral, acidic, or basic? Explain.
3. A solution of hydrogen peroxide is heated, and a gas is produced. Q: Identify the oxidation state of the oxygen in hydrogen peroxide.

**Significant figures**

• **Counting sig figs in reported numbers:**

1. All non-zero numerals are ALWAYS significant.

2. Zeros are frequently significant.

a. middle zeros are significant

b. trailing and leading zeros are not significant

exception: trailing zeros to the right of the decimal

• **Significant figures in calculations:**

Multiplication and division: Result has the same number of sig figs as the lowest number of sig figs in the input.

Addition and subtraction: Result has the shortest number of decimal places as the lowest number of decimal places in the input.

**Mental Math (exponents and pH calculations)**

You will need to be able to do mental math calculations with exponents and logs.

~Exponents: if things have the same base (such as 10), just add the exponents: (Xm)(Xn) = X(m+n)

~For logs (used in pH calculations) you should know how to estimate; there are relationships between pH, [H], pOH, and [OH] that you can use:

pH + pOH = 14 and pH = -log[H]

|  |  |  |  |
| --- | --- | --- | --- |
| pH | [H] | pOH | [OH] |
| 3 | 1 x 10-3 | 11 | 1 x 10-11 |
| 7 | 1 x 10-7 | 7 | 1 x 10-7 |
| 10 | 1 x 10-10 | 4 | 1 x 10-4 |
| 9.7 | 2 x 10-10 | 4.3 | 1x10-4.3 =  5 x 10-5 |

**\*\*\*if the [H] is 1x10-x, the pH = x**

\*\*\*if the [H]=2x10-x, you can estimate the the pH is slightly less than x because a higher concentration means a more acidic pH

**Mixtures**

A 21.84 g mixture of solid silver sulfite and magnesium sulfite is combined with hydrobromic acid with a 19% yield.

1. Calculate the percent composition of the mixture if 3.226 g of solid is produced.
2. How many microliters of liquid were produced?  
   **Gas Law**

This is mostly about equations. The trickiest part is getting the units right before you plug in numbers. ALL TEMPS MUST BE IN KELVIN. The other units depend on the equation. Units are really important for the ideal gas law, the van der waals equation, and the root-mean-square speed equation. Know what conditions gases behave nonideally at.

1986 B

Three volatile compounds X, Y, and Z each contain element Q. The percent by weight of element Q in each compound was determined. Some of the data obtained are given below.

Compound Percent by Weight of Element Q Molecular Weight

X 64.8% ?

Y 73.0% 104.

Z 59.3% 64.0

(a) The vapor density of compound X at 27 degrees Celsius and 750. mm Hg was determined to be 3.53 grams per liter. Calculate the molecular weight of compound X.

(b) Determine the mass of element Q contained in 1.00 mole of each of the three compounds.

(c) Calculate the most probable value of the atomic weight of element Q.

(d) Compound Z contains carbon, hydrogen, and ele-ment Q. When 1.00 gram of compound Z is oxi-dized and all of the carbon and hydrogen are con-verted to oxides, 1.37 grams of CO2 and 0.281 gram of water are produced. Determine the most probable molecular formula.

BONDING Answers

1.D 2.C 3.A 4.A 5.B 6. D 7.C 8. D

1973D Answer:

In order to have a dipole moment (i.e., to be a polar molecule) a molecule must have polar bonds and must have a molecular geometry which is not symmetrical.

In CH2F2 the C‑F and C‑H bonds are polar and the molecule is not symmetrical; therefore, the molecules is polar and would show a dipole moment.

In CF4 the C‑F bonds are polar, but the molecule is symmetrical; therefore, the molecule is non‑polar and would not show a dipole moment.

1982 Answer:



(b) CO has the shortest bond because there is a triple bond. **OR** because there is the greatest number of electrons between C and O in CO.

© CO32‑ trigonal planar (planar and triangular). C bonding is *sp*2 hybrid – or – C has three bonding pairs and no lone pair.

CO2 linear. C bonding is *sp* hybrid – or – C has two bonding pairs and no lone pairs – or – CO2 is nonpolar and must be linear.

CO linear. Two atoms determine a straight line.

1992 D Answer:

(a) K conducts because of its metallic bonding – or ‑ sea of mobile electrons (or free electrons). KNO3 does not conduct because it is ionically bonded and has immobile ions (or immobile electrons).

(b) SbCl3 has a measurable dipole moment because it has a lone pair of electrons which causes a dipole – or – its dipoles do not cancel – or – it has a trigonal pyramidal structure – or – a clear diagram illustrating any of the above.

© CBr4 boils at a higher temperature than CCl4 because it has stronger intermolecular forces (or van der Waal or dispersion). These stronger forces occur because CBr4 is larger and/or has more electrons than CCl4.

(d) NaI has greater aqueous solubility than I2 because NaI is ionic (or polar), whereas I2 is non‑polar (or covalent). Water, being polar, interacts with the ions of NaI but not with I2. (Like dissolves like accepted if polarity of water is clearly indicated.)

**EQUILIBRIUM Answers**

1.D 2.D 3.D 4.E

**1977 D Answer:**

(a) As volume decreases, pressure increases and the reaction shifts in the direction of fewer molecules (less volume; more SO3) to relieve the stress. Value of Keq does not change.

(b) Additional O2 disturbs the equilibrium and SO3 is formed to relieve the stress. Value of Keq does not change.

© Increase in temperature shifts the reaction to the left to “use up” some of the added heat. Less SO3 remains. Value of Keq decreases due to the relative greater increase in the rate of the endothermic reaction (reaction to the left).

**1995 A Answer:**

(a) CO = f(0.55 mol, 1.6 mol) = 0.34

(b) *Kc* = ([H2O][CO])/([H2][CO2]) = (0.550.55)/(0.200.30) = 5.04

© since Δn = 0, *Kc* = *Kp*

(d) [CO] = 0.55 – 30.0% = 0.55 – 0.165 = 0.385 M

[H2O] = 0.55 – 0.165 = 0.385 M

[H2] = 0.20 + 0.165 = 0.365 M

[CO2] = 0.30 + 0.165 = 0.465 M

K = (0.385)2/(0.3650.465) = 0.87

1. let *X* = Δ[H2] to reach equilibrium

[H2] = 0.50 mol/3.0L - X = 0.167 – *X*

[CO2] = 0.50 mol/3.0L - X = 0.167 – *X*

[CO] = +*X* ; [H2O] = +*X*

K = *X*2/(0.167 – *X*)2 = 5.04 ; *X* = [CO] = 0.12 M

**SOLUTIONS Answers**

1.) E 2.) E 3.) C

**1975 D Answer:**

An alcohol-water solution has a higher than normal (pure water) vapor pressure because alcohol is a volatile solute and contributes substantially to the vapor of the solution. The higher the vapor pressure, the lower the boiling point. A salt-water solution has a lower than normal vapor because salt is a non-volatile solute and solute-solvent interaction decrease the vapor of the solution, the lower the vapor pressure, the higher the boiling point.

**1976 B Answer:**

* + - 1. 



(b) P1 = (P)(*X*1)

mol ions = (2)(4.67 mol) = 9.34 mol

1 kg water = 55.6 mol water



P1= (29.8 mm Hg)(0.856) = 25.5 mm Hg

© Assume no dissociation.

T = kf*m* = (1.86)(4.67) = 8.69C

i = 15.3 / 8.69 = 1.76

(1.76 – 1.00)(100) = 76% dissociated

**1990 A Answer:**

(a) Fe(OH)2  Fe2+ + 2 OH-

(b) 

= 1.59x10-5 M = [Fe2+]

= 3.18x10-5 M = [OH-]

Ksp = [Fe2+][OH-]2 = (1.59x10-5)(3.18x10-5)2

= 1.61x10-14

© 

pH = -log[H+] = 9.50

OR

pOH = -log[OH-] = -log(3.18x10-8) = 4.50

pH = 14 – pOH = 9.50

(d) 50.0 mL of 3.00x10-3 M Fe2+ diluted of 100.0 mL = 1.50x10-3 M Fe2+

50.0 mL of 4.00x10-6 M OH- diluted of 100.0 mL = 2.00x10-6 M OH-

*Q* = [Fe2+][OH-]2 = (1.50x10-3)(2.00x10-6)2

= 6.00x10-15

Precipitate will NOT form since *Q* < Ksp

**1995 D Answer:**

(a) Entropy increases. At the same temperature, liquids and solids have a much lower entropy than do aqueous ions. Ions in solutions have much greater “degrees of freedom and randomness”.

(b) *Ksp* value decreases. *Ksp* = [Pb2+][I-]2. As the temperature is decreased, the rate of the forward (endothermic) reaction decreases resulting in a net decrease in ion concentration which produces a smaller *Ksp* value.

© No effect. The addition of more solid PbI2 does not change the concentration of the PbI2 which is a constant (at constant temperature), therefore, neither the rate of the forward nor reverse reaction is affected and the concentration of iodide ions remains the same.

(d) Δ*G* increases. Increasing the concentration of Pb2+ ions causes a spontaneous increase in the reverse reaction rate (a “shift left” according to LeChatelier’s Principle). A reverse reaction is spontaneous when the *G*>0.

**ACIDS&BASES Answers**

1.E 2.C 3.C 4.B 5.E

**1989 A Answer:**

(a) (0.2211M)(0.03523L) = 7.789x10-3 mol

1.3717g/7.789x10-3 mol = 176.1g/mol

(b) at pH 4.23, [H+] = 8.0x10-8M







© A- + H2O ⬄ HA + OH-



(d) at equiv. Pt.



[OH-]2 = (1.3x10-10)(9.14x10-2) = 1.2x10-11

[OH-] = 3.4x10-6M

pOH =-log(3.4x10-6) =5.47; pH = (14-5.47)= 8.53

**1992 D Answer:**

(a) Best conjugate pair: H2PO4-, HPO42-. When 7.2 = pH = pKa for this pair when [H2PO4-] = [HPO42-].

(b) Dissolve equal moles (or amounts) of H2PO4-, and HPO42- (or ppropriate compounds) in water.

© pH not changed. Capacity of buffer would increase because there are more moles of conjugate acid and conjugate base to react with added base or acid.

(d) Add strong base to salt of conjugate acid **OR** add strong acid to salt of conjugate base.

Add 1 mole conjugate acid to 1/2 mole strong base **OR** 1 mole conjugate base to 1/2 mole strong acid.

**OR**

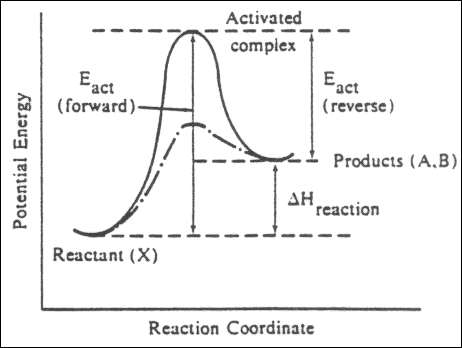
Use pH meter to monitor addition of strong base to conjugate acid **OR** strong acid to conjugate base.

**KINETICS Answers**

1.B 2.B

**1980 D Answer:**

4 points, At 1/2 point each: Curve shape, labeled axes, reactant energy, product energy, energy of activated complex, enthalpy change, activation energy (forward), and activation energy (reverse).



(b) 2 points, Catalyzed path (dotted line on diagram)

Catalyst role: changes mechanism, or increases fraction of molecules with sufficient energy to react.

© 2 points, The ratio, kf / kr increases with temperature, because...

kf / kr = K and LeChatelier shift **OR** Boltzmann distribution graph **OR** T[delta]S changes for net reaction influencing [delta]G **OR** kf increased more than kr for endothermic reaction.

**1983 Answer:**

three points

Plot ln k or log k vs 1/T

Eact = - R (slope) or – 2,303 R (slope)

For partial credit, if the 2-point equation is given for the activation evergy, the student may receive a point. A student may also receive a point if it is stated that k is plotted vs 1/T or if ln K or log k is plotted vs T.

b) five points

Plot ln PA or log PA vs time.

Plot 1/PA vs time.

If ln PA vs time is linear, the reaction is first order. If 1/PA vs time is linear, the reaction is second order.

If first order, slope = - k1 or – k1 / 2.303.

If second order, slope = k2.

**1994 Answer**

three points (point for each order must include justification)

From exps. 1 and 2: doubling [H2] while keeping [NO] constant doubles the rate, therefore the reaction is first order in [H2].

From exps. 3 and 4; doubling [NO] while keeping [H2] constant quadruples the rate, therefore the reaction is second order in [NO].

Rate = k [H2] [NO]2

Note: full credit is earned for the rate expression as long as it is consistent with orders described by student.

b) two points (one for value and one for units)

k= Rate / ([H2] [NO]2)

From exp. 1: k = 1.8 x 10¯4 M/min / [(1.0 x 10¯3 M) (6.0 x 10¯3 M)2]

= 5.0 x 103 M¯2 min¯1

Note: the unit is often written as L2 mol¯2 min¯1

c) one point

Stoichiometry: NO : H2 is 1:1

When 0.0010 mole of H2 had reacted , it must have reacted with 0.0010 mole NO; thus [NO] remaining = 0.0060 – 0.0010 = 0.0050 M

d) three points

(i) For I : Keq = [N2O2] / [NO]2

For II: Rate= k[H2] [N2O2]

[N2O2] = Keq [NO]2

Rate = k’ [H2][NO]2

Note: there must be some clear algebraic manipulation showing that [N2O2] is proportional (NOT equal) to [NO]2.

Step II is the rate determining step.

(ii)

I: NO + NO -🡪 N2O2  
II: N2O2 + H2 -🡪 H2O + N2O  
III: N2O + H2 -🡪 N2 + H2O  
I + II + III: 2NO + 2H2 -🡪 N2 + 2 H2O

**THERMO Answers**

1.C 2.E 3.B 4.A 5.B 6.C 7.D

**1972 Answer:**

(a) 

= [(19.6)(2)+(-70.1)(2)]-[58.6+(-27.1)(2)] cal

= -105.4 cal = -441 J/K

(b) *E*°cell = [+1.07 + (-0.77)] v = 0.30 v

Δ*G*°=-nℑ*E*°=-(2)(96500)(0.30v)=-57900 J/mol

© Δ*H*° = Δ*G*° + TΔ*S*° = 57900 + 298(-441) J

= -73.5 kJ/mol

**1988 D Answer:**

(a) Equipment needed includes a thermometer, and a container for the reaction, preferably a container that serves as a calorimeter, and volumetric glassware (graduated cylinder, pipet, etc.).

(b) Measurements include the difference in temperatures between just before the start of the reaction and the completion of the reaction, and amounts (volume, moles) of the acid and the base.

© Determination of heat (evolved or absorbed): The sum of the volumes (or masses) of the two solutions, and change in temperature and the specific heat of water are multiplied together to determine the heat of solution for the sample used. *Q* = (m)(cp)(T).

Division of the calculated heat of neutralization by moles of water produced, or moles of H+, or moles of OH-, or moles of limiting reagent.

(d) Experimental errors: heat loss to the calorimeter wall, to air, to the thermometer; incomplete transfer of acid or base from graduated cylinder; spattering of some of the acid or base so that incomplete mixing occurred, … Experimenter errors: dirty glassware, spilled solution, misread volume or temperature, …

**NUCLEAR Answers**

1. D 2.C 3.D

**1997 Answer:**

* + - 1. 23494Pu → 42α + 23092U

Due to a printing error, the student’s answer booklet had the Pu-239 isotope. Therefore, the following is a valid response.

23994Pu → 42α + 23592U

(b) This mass defect has been converted into energy. Δ*E* = Δ*mc2*

© An alpha particle, α or He nuclei, has a 2+ charge and would be attracted to the (-) side of the electric field. A beta particle, β, or electron, has a single negative charge and is attracted to the positive side of the electric field, but since it is much lighter and faster than an alpha it would not be as strongly deflected. Gamma, γ, rays are not charged and, therefore, not deflected by the electric field.



(d) The half-life of a radionuclide is independent of its environment. Incineration will neither accelerate its decay nor render it non-radioactive. Half-life is a function of its nucleus, incineration is a function of its electrons.

**LAB Answers**

1. B 2.A 3.B 4.C

**1998 D Answer**

1. • exactly mass a sample of KHP in the Erlenmeyer flask and add distilled water to dissolve the solid.

• add a few drops of phenolphthalein to the flask.

• rinse the buret with the NaOH solution and fill.

• record starting volume of base in buret.

• with mixing, titrate the KHP with the NaOH solution until it just turns slightly pink.

• record end volume of buret.

• repeat to check your results.

(b)  = moles of KHP

since KHP is monoprotic, this is the number of moles of NaOH

 = molarity of NaOH

© 

(d) from the titration curve, at the 12.5 mL volume point, the acid is half-neutralized and the pH = p*K*a. *K*a = 10p*Ka*

(e) Y2- (could it be OH- ?)

**Chemical Reactions Answers**

1. H+ + OH- 🡪 H2O, it would appear yellow
2. C3H8+ 5O2 🡪3CO2 + 4H2O, acidic because the carbon dioxide reacts with the water to form carbonic acid (a weak acid)
3. 2H2O2 🡪 2H2O + O2, oxidation state: -1

**Mixtures Answers**

37% Magnesium sulfite, 61% silver bromide, 432 microliters of water

Ag2SO3 + 2 HBr 🡪 2AgBr(s) + H2O + SO2(19% yield)

MgSO3 + 2 HBr 🡪 MgBr2 (aq)+ H2O + SO2 (19% yield)

~The key here is knowing what is solid. There is only one solid, and you know the mass of this solid. So, perform the following calculation:

? g Ag2SO3 = 3.226 g AgBr

(answer 13.37g) this allows you to calculate the percent silver sulfite; subtract from 100% to get magnesium sulfite percentage

~Since water is made in both reactions, begin with the mass of each solid and use stoichiometry to calculate the microliters of water (155 for the silver and 278 for the magnesium). Then, add them together.

**GAS LAWS ANSWERS**

1986 B Answer:

(a)

= 88.1 g/mol

(b) X Y Z

88.1 g/mol 104 64.0

% Q 64.8 73.0 59.3

g Q 57.1 75.9 38.0

(c) ratio 1.5 2 1

masses must be integral multiples of atomic weight

therefore, 3 4 2

which gives an atomic weight of Q = 19

(d) 1.37 g CO2

= 0.0311 mol C

0.281 g H2O

0.0312 mol H

1.00 g Z is 59.3% Q = 0.593 g Q

therefore, the empirical formula = CHQ, the smallest whole number ratio of moles.

formula wt. of CHQ = 32.0, if mol. wt. Z = 64 then the formula of Z = (CHQ)2 or C2H2Q2