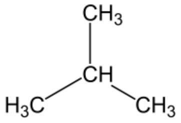
Intermolecular Forces

1. Arrange the following in order of increasing boiling point. Explain your reasoning.

   A) CH_4 B) $CH_3CH_2CH_2CH_3$ C)  D) $CH_3CH_2CH_2Cl$ E) $CH_3CH_2CH_2OH$

2. How much energy is released when 47.5 g of water freezes? (ΔH_{fus} = 6.02 kJ/mol for H_2O)

3. Platinum crystallizes with the face centered cubic unit cell. The radius of a platinum atom is 139 pm. Calculate the edge length of the unit cell and the density of platinum in g/cm^3.

4. NaCl crystalizes in a face centerd cubic lattice of chloride ions, with the smaller sodium ions occupying holes between the chloride ions. How many Cl^- ions are in contact with any single Na^+ ion?
   a. 4
   b. 6
   c. 8
   d. 12

Solutions

1. An aqueous NaCl solution is made using 133 g of NaCl diluted to a total solution volume of 1.00 L. Calculate the molarity, molality, and mass percent of the solution. (Assume the solution has a density of 1.08 g/mL.)

2. A solution contains 55.8 g of glucose ($C_6H_{12}O_6$) in 455 g of water. What is the freezing point and boiling point of the solution?
   For water: f.p. = 0.000°C $K_f = 1.858°C/m$ b.p. = 100.000°C $K_b = 0.512°C/m$

Kinetics

1. For the reaction given below, express the rate of reaction with respect to each of the reactants and products.

$2\ N_2\ (g) + 5\ O_2\ (g) \rightarrow 2\ N_2O_5\ (g)$

2. Given the following experimental data, find the rate law and the rate constant for the reaction:

$NO\ (g) + NO_2\ (g) + O_2\ (g) \rightarrow N_2O_5\ (g)$

Run	$[NO]_0$	$[NO_2]_0$	$[O_2]_0$	Initial Rate ($M \cdot s^{-1}$)
1	0.10 M	0.10 M	0.10 M	2.1×10^{-2}
2	0.20 M	0.10 M	0.10 M	4.2×10^{-2}
3	0.20 M	0.30 M	0.10 M	1.26×10^{-1}
4	0.10 M	0.10 M	0.20 M	2.1×10^{-2}

What is the overall reaction order?

3. Indicate the order of reaction for each of the following observations.
   a. A plot of the concentration of the reactant versus time which yields a straight line.
   b. Reactions having a half-life that is independent of initial concentration.
   c. A plot of the reciprocal of the concentration versus time yields a straight line.

4. Consider the following overall reaction which is experimentally observed to be second order in AB and zero order in C.

   $AB + C \rightarrow A + BC$

   Determine whether the mechanism below is valid for this reaction

   $AB + AB \xrightarrow{k_1} AB + A$ (slow)

   $AB + C \xrightarrow{k_2} AB + BC$ (fast)

5. The rate law for the reaction A + b→ C + D is first order in [A] and second order in [B]. If [A] is halved and [B] is doubled, wthe rate of the reaction will
   a. Remain the same.
   b. Be increased by a factor of 2
   c. Be increased by a factor of 4
   d. Be increased by a factor of 8

Equilibrium

1. Consider the following exothermic reaction:

   $C_2H_4 (g) + Cl_2 (g) \rightleftarrows C_2H_4Cl_2 (g)$

   If you were a chemist trying to maximize the amount of $C_2H_4Cl_2$ produced, which of the following might you try? Assume that the reaction mixture reaches equilibrium.

   A. Increasing the reaction volume
   b. Removing $C_2H_4Cl_2$ from the reaction mixture as it forms.
   c. Lowering the reaction temperature
   d. Adding Cl_2

2. The reversible reaction

   $CO (g) + 2 H_2 (g) \rightleftarrows CH_3OH (g) + \text{heat}$

   is carried out by mixing carbon monoxide and hydrogen gases in a closed vessel under high pressure with a suitable catalyst. After equilibrium established at high temperature and pressure, all three substances are present. If the pressure on the system is lowered, with the temperature held constant, what will be the result?

   a. The amount of CH_3OH will increase.
   b. The amount of CH_3OH will decrease.
   c. The amount of each substance will be unchanged
   d. The amount of each substance will increase.

3. Carbon monoxide gas reacts with hydrogen gas at elevated temperatures to form methanol according to this equation:

   $CO\ (g) + 2\ H_2\ (g) \rightleftarrows CH_3OH\ (g)$ + heat

   When 0.40 mol of CO and 0.30 mol of H_2 are allowed to reach equilibrium in a 1.0 L container, 0.060 mol of CH_3OH are formed. What is the value of K_c?

   a. 0.50 b. 0.98 c. 1.7 d. 5.4

Acid and Base Chemistry

1. Classify each acid as strong or weak. If the acid is weak, write an expression for the acid ionization constant (K_a)

   a. HF b. HCl c. H_2SO_4 d. H_2CO_3

2. Determine the percent of ionization of a 0.225 M solution of benzoic acid (K_a= 6.5 × 10^{-5})?

3. Determine the pH of the following solutions:

   a. 0.0195 M KOH b. 0.318 M KC_6H_5O (K_a phenol = 1.3 × 10^{-10})

Aqueous Ionic Equilibrium

1. Consider a titration of a 35.0 mL sample of 0.175 M HBr is titrated with 0.200 M KOH. Determine:
    a. Initial pH

    b. equivalence volume

    c. pH when 10.0 mL 0.200 M KOH has been added

    d. pH at the equivalence point

    E. pH at 5.0 mL past the equivalence point

    F. Draw a rough graph of what the titration curve expected.

2. If $Q_{sp} > K_{sp}$ is the solution saturated, unsaturated, or supersaturated?

Free Energy and Thermodynamics

1. Calculate ΔS°_{surr} at the given temperature for a reaction with the following conditions:

   ΔH^o_{rxn} = -287 kJ; T = 298 K

2. Determine the value of ΔH^o_{rxn}, ΔS^o_{rxn} and ΔG^o_{rxn} at 25°C and the spontaneity. If nonspontaneous, is it possible that a change in temperature will make it spontaneous? If so, should the temperature be raised or lowered to accomplish spontaneity?

   $3\ H_2\ (g) + Fe_2O_3\ (s) \rightarrow 2\ Fe\ (s) + 3\ H_2O\ (g)$

   ΔH^o_f(kJ/mol): H_2 (g): 0 Fe_2O_3 (s): -824.2 Fe(s): 0, H_2O (g): -241.8

   ΔS^o(J/mol·K): H_2 (g): 130.7 Fe_2O_3 (s): 87.4 Fe(s): 27.3 H_2O (g): 188.8

3. Find the equilibrium constant for the following reaction at 25°C:

   $2\ H_2S\ (g) \leftrightarrows 2\ H_2\ (g) + S_2\ (g)$

   A. ΔG^o_{rxn}= -33.4 kJ/mol b. ΔG^o_{rxn}= 0.0 kJ/mol c. ΔG^o_{rxn}= 79.7 kJ/mol

Electrochemistry

1. Balance the following redox reaction in acidic solution:

   BrO_3^- (*aq*) + N_2H_4 (*g*) → Br^- (*aq*) + N_2 (*g*)

2. Sketch the cell for the following reaction:

   Cr (*s*) + Fe^{3+} (*aq*) → Fe^{2+} (*aq*) + Cr^{3+} (*aq*)

3. Express the following reaction in cell notation:

   $2\ Ag^{+}\ (aq) + Pb\ (s) \rightarrow 2\ Ag(s) + Pb^{2+}\ (aq)$

4. Balance the following reaction in basic solution:

   $Al\ (s)\ +\ MnO_4^{-}\ (aq)\ \rightarrow\ MnO_2\ (s) +\ Al(OH)_4^{-}\ (aq)$

5. Calculate E^{o}_{cell} for the following redox reaction and determine spontaneity.

   $2\ Cu\ (s) +\ Mn^{2+}(aq) \rightarrow 2\ Cu^{+}\ (aq) +\ Mn\ (s)$

6. Which of the following metal cations is the best oxidizing agent? Why?

   Pb^{2+}, Cr^{3+}, Fe^{2+}, Sn^{2+}

Nuclear Chemistry

1. One of the nuclides in spent nuclear fuel is U-235, an alpha emitter with a half-life of 703 million years. How long would it take for the amount of U-235 to reach one-eighth of its initial mass? What is the order of this process?

2. Write a nuclear equation for the fusion of two H-2 atoms to form He-3 and one neutron.

3. If 1.0 g of matter were converted to energy, how much energy would be formed?

Answer Key:

Intermolecular forces

1. A<C<B<D<E. Boiling point increases with increasing intermolecular forces. The molecules increase in their intermolecular forces as follows: A - dispersion forces; forces (broader electron cloud); C - dispersion forces over a condensed area. B - stronger dispersion D - dispersion forces and dipole-dipole interactions; E - dispersion forces, dipole-dipole interactions, and hydrogen bonding.

2. 15.9 kJ

$$47.5\ H_2O \times \frac{1\ \text{mol}\ H_2O}{18.016\ \text{g}\ H_2O} \times \frac{6.02\ \text{kJ}}{1\ \text{mol}\ H_2O} = 15.9\ \text{kJ}$$

3. l=393 pm, d=21.3 g/cm^3

$$l = 2\sqrt{2} * r = 139 \times 10^{-12} * 2\sqrt{2} = 393\ \text{pm}$$

$$V = l^3 = \left(\frac{393*10^{-12}}{10^{-2}}\right)^3 = 6.0698 * 10^{-23}\text{cm}^3$$

$$\text{mass of unit cell} = \frac{195.08\text{ g}}{6.022*10^{23}\text{ atoms}} = \frac{3.239*10^{-22}\text{ g}}{\text{atom}} \times \frac{4\text{ atoms}}{1\text{ cell}} = 1.296*10^{-21}\text{g}$$

$$\text{Density}=\frac{\text{mass}}{\text{Volume}} = \frac{1.296*10^{-21}}{6.0698*10^{-23}} = 23.3\,\frac{\text{g}}{\text{cm}^3}$$

4. b.

Solutions

1. moles NaCl = 133g NaCl / 58.44 g/mol = 2.28 mol

   M = mol/L 2.28 mol/ 1 L = 2.28M,

   m = mol solute / kg solvent = 2.28 / (1.080 kg -.133 kg) = 2.41 *m*,

   % mass = g solute/grams solution * 100% = .133/1.08 * 100% = 12.3% by mass

2. molar mass = 55.8/180.156 g/mol = 0.3097

   0.3097/0.455 = 0.6807 *molal*

   $\Delta \mathrm{T} = m \times K_f = .6807 * 1.86$

   $\Delta \mathrm{T} = m \times K_b = .6807 * 0.512$

   f.p. = -1.27 °C, b.p. = 100.349 °C

Kinetics

1. $2\ N_2\ (g) + 5\ O_2\ (g) \rightarrow 2\ N_2O_5\ (g)$

   $\text{Rate} = -\frac{1}{2}\frac{\Delta[\mathrm{N_2}]}{\Delta t} = -\frac{1}{5}\frac{\Delta[\mathrm{O_2}]}{\Delta t} = +\frac{1}{2}\frac{\Delta[\mathrm{N_2O_5}]}{\Delta t}$

2. Rate =k [NO][NO_2]

   $\frac{Rate}{[\mathrm{NO}][\mathrm{NO_2}]} = \text{k} = 2.1\ \text{m}^{-1}\cdot\text{s}^{-1}$

   2nd order reaction.

3. a. zero order b. first order c. second order

4. Yes it's valid

5. b.

Equilibrium

1. B, C, d.

2. b.

3. $0.060/(0.4*0.3^2)=1.66666 \sim 1.7$ C.

Acid and Base Chemistry

1. Classify each acid as strong or weak. If the acid is weak, write an expression for the acid ionization constant (K_a). If K_a is available, it is a weak acid.

   a. HF: weak acid

   $HF\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + F^-\ (aq)$

   $K_a = \frac{[H3O^+][F^-]}{[HF]}$

   b. HCl: strong acid
   c. H_2SO_4: strong acid
   d. H_2CO_3:

   $H_2CO_3\ (aq) + H_2O\ (l) \rightarrow H_3O^+\ (aq) + HCO_3^-\ (aq)$

   $K_a = \frac{[H3O+][HCO_3^-]}{[H2CO_3]}$

2. Find the % ionization of a 0.225 M benzoic acid solution.

H_2O	$C_6H_5CO_2H$	H_3O^+	$C_6H_5CO_2^-$
I	0.225M	0	0
C	-x	+x	+x
E	0.225-x	X	X

$K_a = \frac{[H3O+][HSO3-]}{[H2SO3]} = \frac{[x\text{^}2]}{[0.225-x]} = 6.5 \times 10^{-5}$

Assume x is small. x= .00382

Get percent ionization.

% ionization = $\frac{concentration\ of\ ionized\ acid}{initial\ concentration\ of\ acid} \times 100\% = \frac{0.00383}{0.225} \times 100\% = 1.70\%$

3. a. pH = - log(H_3O^+) = - log (0.0195) = 12.29

   b. Get $K_b = \frac{K_w}{K_a} = \frac{1\times10^{-14}}{1.3\times10^{-10}} = 7.7 \times 10^{-5}$. Ice table to get x = 4.95×10^{-3}. pOH = -log (x) = 2.31,

   pH = 14- pOH = 14- 2.31 = 11.69

Aqueous Ionic Equilibrium

1. a. HBr is a strong acid, disassociates completely. pH = -log $[H_3O^+]$

   pH = -log 0.175 = 0.757

   b. Volume for equivalence:

   35.0 mL HBr >> 0.035 L and .175 M HBr * .0350 L = 0.006125 mol HBr

   Need mol acid to = mol base

   0.006125 mol KOH / 0.2M KOH = 0.030625 L KOH * 1000 = 30.6 mL

c. pH after 10 mL base added:

   get moles base: 0.01 L * .2 = .0002 mol KOH

   0.006125 mol HBr - .0002 mol KOH = 0.004125 mol HBr left

   Need new molarity. 0.004125 / .045 L = .0916667 M

   H & H equation: pH = log $\frac{[base\ added]}{[remaining\ acid]}$

   pH =- log $.0916667 = 1.038$

d. pH @ equivalence point:

   since strong acid/base titration pH = 7

E. pH 5 mL past equivalence point:

   all of the acid has been made into water by the base.

   .2 M * 0.005 L = 0.0010 moles base.

   Molarity = .00010 moles / .0706L = .14164 M

   $[H_3O^+]= K_w/[OH^-]= 1*10^{-14}/.14164 = 8.69565 *10^{-14}$

   pH = -log ($8.69565 *10^{-14}$) = 13.06

F. pH vs. volume graph will be nearly linear and then have a sharp upward slope near equivalence volume. Equivalence pH = 7. The graph will start low at a low pH and end at a high pH.

2. The solution is supersaturated. Solid will begin to precipitate out of solution when Q > K_{sp} or a seed crystal could cause a precipitate to form if the supersaturated solution was heated to allow increased solubility.

Free Energy and Thermodynamics

Spontaneity:

ΔH	ΔS	High Temp	Low Temp
-	+	spontaneous	Spontaneous
+	-	nonspontaneous	nonspontaneous
-	-	nonspontaneous	Spontaneous
+	+	spontaneous	nonspontaneous

Mathematically:

$$\Delta G_f^o = \Delta H_f^o - \mathrm{T}\Delta S_f^o$$

If ΔH is negative and you are subtracting a positive number, the result must be negative (spontaneous).

If ΔH is positive and you are subtracting a negative number (+# - -#), the result must be positive (nonspontaneous).

1. $\Delta S^o_{surr} = \frac{-\Delta H^o_{sys}}{T}$ => $\Delta S^o_{surr} = -\frac{-287000}{298} = 963\ \frac{J}{K}$

2. $\Delta H^o_{rxn} = \sum n_p \times \Delta H^o_f(products) - \sum n_r \times \Delta H^o_f(reactants)$

   ΔH^o_{rxn} = +98.8 kJ

   $\Delta S^o_{rxn} = \sum n_p \times \Delta S^o_f(products) - \sum n_r \times \Delta S^o_f(reactants)$

   ΔS^o_{rxn} = +141.5 J/K T= 25°C + 273.15 = 298 K

   $\Delta G^o = \Delta H^o_{rxn} - T\,\Delta S^o_{rxn}$ ΔG^o = 98800 J - (298 K) (141.5$\frac{J}{K}$) = +56.6 kJ. Reaction is non-spontaneous. The reaction can be made spontaneous by increasing the temperature.

   $\Delta G^o_{rxn} = \sum n_p \times \Delta G^o_f(products) - \sum n_r \times \Delta G^o_f(reactants)$

   $\Delta G^o_{rxn} = [2(0.0) + 1(79.7)] - [2(-33.4)]$= +146.5 kJ

3. $\Delta G^o_{rxn} = -RT\ln K$ a. $K_{eq} = e^{\frac{-\Delta G^o_{rxn}}{RT}} = e^{-\frac{-33400J}{(8.314\frac{J}{K\cdot mol})(298K)}} = 7.16 \times 10^5$

   b. $K_{eq} = e^{\frac{-\Delta G^o_{rxn}}{RT}} = e^{-\frac{0J}{(8.314\frac{J}{K\cdot mol})(298K)}} = 1$ c. $K_{eq} = e^{\frac{-\Delta G^o_{rxn}}{RT}} = e^{-\frac{79700J}{(8.314\frac{J}{K\cdot mol})(298K)}} = 1.07 \times 10^{-14}$

Electrochemistry

1. BrO_3^- (aq) + N_2H_4 (g) → Br^- (aq) + N_2 (g)

   ½ RXNS:

   BrO_3^- (aq) → Br^- (aq)

   N_2H_4 (g) → N_2 (g)

   Balance O's, Add H_2O:

   BrO_3^- (aq) → Br^- (aq) + 3 H_2O (l)

   Balance H w/H^+:

   6H^+ (aq) + BrO_3^- (aq) → Br^- (aq) + 3 H_2O (l)

   N_2H_4 (g) → N_2 (g) + 4 H^+ (aq)

   Add electrons:

   6H^+ (aq) + BrO_3^- (aq) + 6 e^- → Br^- (aq) + 3 H_2O (l)

   N_2H_4 (g) → N_2 (g) + 4 H^+ (aq) + 4 e^-

   Equalize electrons:

   12H^+ (aq) + 2BrO_3^- (aq) + 12 e^- → 2Br^- (aq) + 6 H_2O (l)

$3N_2H_4$ (g) → $3N_2$ (g) + 12 H^+ (aq) + 12 e^-

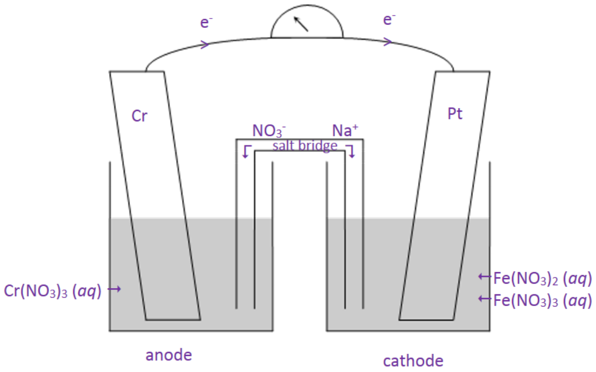
Add ½ rxns:

$3N_2H_4$ (g) + 12H^+ (aq) + 2BrO_3^- (aq) + 12 e^- → 2Br^- (aq) + 6 H_2O (l) + $3N_2$ (g) + 12 H^+ (aq) + 12 e^-

Cancel stuff (12 H^+, 12 e^- leaves):

$3N_2H_4$ (g) + 2BrO_3^- (aq) → 2Br^- (aq) + 6 H_2O (l) + $3N_2$ (g)

2.



3. 2 Ag^+ (aq) + Pb (s) → 2 Ag(s) + Pb^{2+} (aq)   in cell notation:

Pb (*s*)| Pb^{2+} (*aq*) || Ag^+ (*aq*) |Ag(*s*)

4. Al (*s*) +MnO_4^- (*aq*) → MnO_2(*s*) + $Al(OH)_4^-$ (*aq*)

Two ½ RXNS: MnO_4^- (aq) → MnO_2 (s) ***AND*** Al(s) → $Al(OH)_4^-$ (aq)

Balance Everything but O and H:
already done
Balance O by adding H_2O:

MnO_4^- (aq) → MnO_2 (s) + 2 H_2O (l)

Al(s) + 4 H_2O (l) → $Al(OH)_4^-$ (aq)

Balance H w/H^+:

4 H^+ (aq) + MnO_4^- (aq) → MnO_2 (s) + 2 H_2O (l)

Al(s) + 4 H_2O (l) → $Al(OH)_4^-$ (aq) + 4 H^+ (aq)

Neutralize H+ with OH^-, adding the same number of OH- to each side of the equations:

4 OH^- (aq) + 4 H^+ (aq) + MnO_4^- (aq) → MnO_2 (s) + 2 H_2O (l) + 4 OH^- (aq)

4 OH^- (aq) + Al(s) + 4 H_2O (l) → $Al(OH)_4^-$ (aq) + 4 H^+ (aq) + 4 OH^- (aq)

Cancel waters:

$2\ H_2O\ (l) + MnO_4^-\ (aq) \rightarrow MnO_2\ (s) + 4\ OH^-\ (aq)$

$4\ OH^-\ (aq) + Al(s) \rightarrow Al(OH)_4^-\ (aq) + 2\ H_2O\ (l)$

Equalize charge by adding electrons:

$3\ e^- + 2\ H_2O\ (l) + MnO_4^-\ (aq) \rightarrow MnO_2\ (s) + 4\ OH^-\ (aq)$

$4\ OH^-\ (aq) + Al(s) \rightarrow Al(OH)_4^-\ (aq) + 3\ e^-$

Add ½ rxns:

$3\ e^- + 2\ H_2O\ (l) + MnO_4^-\ (aq) + 4\ OH^-\ (aq) + Al(s) \rightarrow MnO_2\ (s) + 4\ OH^-\ (aq) + Al(OH)_4^-\ (aq) + 3\ e^-$

Cancel stuff (4 OH$^-$ and 3 e$^-$ leaves):

$2\ H_2O\ (l) + MnO_4^-\ (aq) + Al(s) \rightarrow MnO_2\ (s) + Al(OH)_4^-\ (aq)$

5. E^o_{cell} and spontaneity for:

$2\ Cu\ (s) + Mn^{2+}(aq) \rightarrow 2\ Cu^+\ (aq) + Mn\ (s)$

2 ½ rxns w/electrons:

$2\ Cu\ (s) + 2\ e^- \rightarrow 2\ Cu^+\ (aq)$

$Mn^{2+}\ (aq) \rightarrow Mn\ (s) + 2\ e^-$

Look up potentials:

Mn reduced, $E°_{red} = -1.18$ V

Cu oxidized, $E°_{ox} = -E°_{red} = -0.52$V

$E°_{cell} = E°_{ox} + E°_{red} = -1.70$V

Negative $E°_{cell}$, nonspontaneous.

6. Pb^{2+} is the strongest oxidizing agent because it has the highest E° (most positive in the table).

Relevant equation:

$\Delta G = -nFE^o_{cell}$ F = 96,485 C/mol e$^-$

Nuclear Chemistry

1. 2.11×10^9 yr, 1st order.
2. ${}^{2}_{1}H + {}^{2}_{1}H \rightarrow {}^{3}_{2}He + {}^{1}_{0}n$
3. $E = mc^2$, $c = 2.998*10^8$

   $1/1000 * (2.998*10^8)^2 = 8.988*10^{13}$ J $= 9.0 \times 10^{13}$ J