KEY

FREE RESPONSE

1. Answer the following questions about the analysis of iron-containing compounds using potassium permanganate solution.
   a. Write the balanced equation in ACID solution for the reaction below:

$Fe^{2+} + MnO_4^{1-} \rightarrow Fe^{3+} + Mn^{2+}$

$(Fe^{+2} \rightarrow Fe^{+3} + 1e^-)\ 5$

$5e^- + 8H^{+1} + MnO_4^- \rightarrow Mn^{+2} + 4H_2O$

$$5Fe^{+2} + 8H^{+1} + MnO_4^- \rightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O$$

   b. To standardize a potassium permanganate solution, a 0.250 g sample of FAS (iron (II) ammonium sulfate hexahydrate; molar mass: 342 g) is dissolved in 25.00 mL distilled water, then acidified with sulfuric acid. The solution is then titrated with 35.00 mL potassium permanganate solution from a burette until a pale persistent purple color is attained. Calculate the molarity of the potassium permanganate solution.

$$\frac{0.250\,g}{342\,\frac{g}{mol}} = 7.31\times10^{-4}\,mol\,Fe^{+2}\left(\frac{1\,MnO_4^-}{5\,Fe^{+2}}\right) = 1.46\times10^{-4}\,mol\,MnO_4^-$$

$$\frac{1.46\times10^{-4}\,mol}{0.0350\,L} = 0.00418\,M\ KMnO_4$$

   c. The standardized potassium permanganate solution is then used to titrate a solution made by dissolving a 0.500 g sample of a mixture of iron (II) sulfate and sodium sulfate in 50.00 mL dilute sulfuric acid. A total of 10.21 mL of potassium permanganate solution is required to reach the pale purple endpoint. What is the mass percent of iron (II) sulfate in the original mixture?

$$0.01021\,L \times 0.00418\,\frac{mol}{L} \times 5 \times 151.85\,\frac{g}{mol} = 0.0327\,g\ FeSO_4$$

$$\frac{0.0327\,g}{0.500\,g} \times 100 = 6.48\%$$

   d. Would would the effect, if any, on the value for the reported standard molarity of potassium permanganate if the following errors were made? Explain each of your three answers.
      i. Some drops of water remained in the burette after cleaning but before the permanganate solution was added to the burette.

Dilution → fewer moles MnO_4^- → less FAS needed to endpt → lower MOLARITY OF $KMnO_4$ standard.

      ii. The student neglected to run some permanganate solution through the tip of the burette before taking the initial reading.

IF "AIR" BUBBLE → DELIVERED VOLUME WOULD BE LESS THAN ACTUAL READING, APPARENT [$KMnO_4$] WOULD BE LOWER. ie. SEEMS LIKE IT TOOK MORE MnO_4^-

      iii. The student's lab partner spilled some FAS after weighing it but before titration.

MORE FAS SOLUTION NEEDED FOR TITRATION GIVEN ASSUMPTION THAT [FAS] IS STILL THE SAME, [$KMnO_4$] WOULD SEEM HIGHER.

2. Periodic Relationships

a. Ionization Energies, (kJ / mol)

	Na	Mg	Al
First Ionization Energy	496	738	578
Second Ionization Energy	4,560	1,450	1,820
Third Ionization Energy	6,917	7,730	2,750

i. The second ionization for each element is greater than the first ionization energy for that element. Explain.

Remove 1e⁻, repulsion/shielding decrease, electron cloud shrinks. Valence e⁻ closer to nucleus, greater Zeff, stronger attraction (Coulomb's Law) more energy required to remove 2nd e⁻.

ii. The difference between the first and second ionization energies is much greater for Na than for Mg. Explain.

Na $1s^2 2s^2 2p^6 3s^1$ Mg $1s^2 2s^2 2p^6 3s^2$
2nd electron comes from core/inner shell where Zeff is greater requiring more energy.

b. Atomic / Ionic Radius, (nm)

$_{16}S$	$_{16}S^{2-}$	$_{20}Ca$	$_{20}Ca^{2+}$
0.104	0.184	.197	0.099

i. The radius of $_{16}S$ is less than the radius of $_{16}S^{2-}$. Explain.

same protons - More electrons = greater repulsion → cloud expands

ii. The $_{16}S^{2-}$ and $_{20}Ca^{2+}$ are isoelectronic species. However, the radius of $_{16}S^{2-}$ is greater than the radius of $_{20}Ca^{2+}$. Explain.

Both have same electron configuration & shielding, but Ca has 20 protons vs. S 16 protons. Greater nuclear charge → greater Zeff → stronger Force (Coulomb) pulls valence shell closer,

3. Answer all four questions about the burning of octane.

$$C_8H_{18(\ell)} + \frac{25}{2}O_{2(g)} \rightarrow 8CO_{2(g)} + 9H_2O_{(g)} + \text{heat}$$ EXO

The combustion reaction above is the source of the energy produced by the burning of octane in an automobile engine. This reaction is spontaneous at 298 K.

a. Predict the sign of ΔS in the reaction. Explain.

$\Delta S = +$ L → GAS, MORE TOTAL MOLES OF GAS

b. Predict the sign of ΔG for this reaction at 298 K. Explain.

$\Delta G = \Delta H - T\Delta S$ (ΔH: −, ΔS: +) $\Delta G = -$ Since $\Delta H = -$, $\Delta H = +$

c. $\Delta H^o_{f,\,CO_2\,(g)} = -393.5$ kJ/mol; $\Delta H^o_{f,\,CO\,(g)} = -110.5$ kJ/mol

If some of the reactants were converted to CO rather than CO_2, how would the total amount of energy produced be affected? Explain.

DECREASED. $\Delta H_f^o\, CO_2 > \Delta H_f^o\, CO$, SO LESS ENERGY PRODUCED.

d. If this reaction were carried out at a temperature greater than 298 K, for which of the three parameters, ΔH, ΔG, or ΔS, would the change in value have the greatest magnitude? Explain.

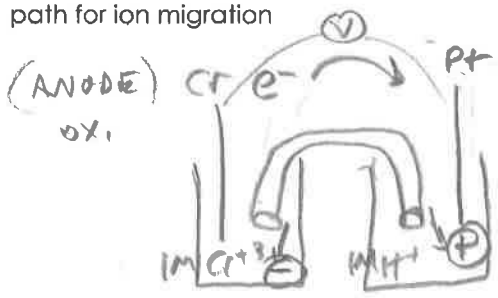
$\Delta G = \Delta H - T\Delta S$ ΔH, ΔS ~ CONSTANT OVER T RANGE

SINCE ΔS is multiplied by T, Greater T means TΔS increases & ΔH − TΔS will have a larger change in magnitude.

4. Answer the following questions about a chromium/hydrogen electrochemical cell.
   a. Make a labeled sketch of an electrochemical cell using a standard Cr/Cr^{3+} half cell connected to a standard hydrogen half-cell. Your labels should include:
      i. anode
      ii. cathode
      iii. chemical components and concentration(s) in the chromium half cell
      iv. direction of electron flow in the external circuit
      v. path for ion migration

$Cr^{+3} + 3e^- \rightarrow Cr \quad E^0 = -0.73V$

$2H^{+1} + 2e^- \rightarrow H_2 \quad E^1 = 0$



   b. Write the half reactions and the balanced overall equation for this cell.

$(Cr \rightarrow Cr^{+3} + 3e^-)2 \qquad 2Cr + 6H^{+1} \rightarrow 2Cr^{+3} + 3H_2$

$(2H^+ + 2e^- \rightarrow H_2)3$

   c. Calculate the voltage for this standard cell.

$E_{cell} = E_{cat} - E_{an} = 0 - (-0.73) =$ **0.73V**

   d. Calculate the voltage when the concentration of Cr^{3+} is 0.050 M.

$$E = E^0 - \frac{0.0592}{n} \log \frac{[Cr^{+3}]^2}{[H^+]^6}$$

$$= 0.73V - \frac{0.0592}{6} \log \frac{(0.05)^2}{(1)^6}$$

$$= \boxed{0.76\,V}$$

5. Methylamine, CH_3NH_2, is an organic base, accepting a proton from water to form the methylammonium ion. The value of K_{eq} for this system is 4.0×10^{-4} at 298 K.

a. Write the chemical equation for the equilibrium as described above.

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^{+1} + OH^-$$

b. Calculate the concentration of hydroxide ions in a 0.25 M solution of methylamine. 5% rule

$$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]} \qquad \frac{x^2}{0.25 - x} = 4 \times 10^{-4} \qquad x = [OH^-] = \boxed{0.010\,M}$$

c. How is the equilibrium affected when solid NaOH is added to a solution of methylamine? Calculate the $[CH_3NH_3^{1+}]$ when 0.020 mol OH^{1-} is added to 500. mL of 0.25 M methylamine, CH_3NH_2. (Assume no change in volume.)

SHIFT LEFT (LESS IONIZATION)

$$[CH_3NH_3^{+1}] = x = \boxed{0.0023\,M}$$

d. A buffer solution is prepared that is 0.20 M in $CH_3NH_3^{1+}$ and 0.25 M in CH_3NH_2. Calculate the pH of this solution.

$$K_a = \frac{K_w}{K_b} = 2.5 \times 10^{-11}$$

$$pH = pK_a + \log \frac{[CH_3NH_2]}{[CH_3NH_3^{+1}]} = 10.6 + \log\left(\frac{.25}{.20}\right) = \boxed{10.7}$$

e. Calculate the number of moles of H^{1+} that must be added to 200. mL of the solution in part (d) in order to change the pH to 10.00.

$$10 - 10.7 = \log \frac{[CH_3NH_2]}{[CH_3NH_3^+]} \qquad \frac{[CH_3NH_2]}{[CH_3NH_3^+]} = 0.20$$

$$\frac{B}{A} = 0.2 \qquad B + A = 0.09$$

$$B = 0.2A \qquad 0.2A + A = 0.09$$

$$A = 0.075 \qquad B = 0.015 \text{ mol}$$

Add $\boxed{0.035 \text{ mol } H^+}$

	CH_3NH_2	+ H^+	→ $CH_3NH_3^{+1}$
in 200 mL	0.05 mol	0.035	0.04 mol
	− 0.035		+ 0.035

c)

	CH_3NH_2	+ H_2O ⇌	$CH_3NH_3^+$	+ OH^-
I	0.25 M		0	0.04 M
C	− x		+ y	+ x
E	0.25 − y		x	0.04 + x

$$4 \times 10^{-4} = \frac{x(0.04 + x)}{0.25 - x}$$

5% rule $x = 0.007$ 10% NO GOOD!

SOLVER $x = 0.0023$

6. Refer to the reaction and data table below:

$$2A_{(g)} + B_{(g)} \rightarrow C_{(g)}$$

Trial	Initial concentration mol L^{-1} [A]	Initial concentration mol L^{-1} [B]	Initial rate of formation of C mol L^{-1} sec^{-1}
I	0.40	0.20	8.0×10^{-4}
II	0.80	0.40	1.6×10^{-3}
III	0.80	0.80	3.2×10^{-3}
IV	0.60	0.60	2.4×10^{-3}
V	0.30	?	4.0×10^{-4}

a. Write the rate law for the reaction above in the form Rate = $k[A]^x[B]^y$ including numerical values for x and y. Explain how you determined the values for exponents x and y.

$R = K[A]^x[B]^y$

constant A; B doubled, Rate doubles so $y = 1$

$\frac{1.6\times10^{-3}}{8\times10^{-4}} = \frac{K}{K}\left(\frac{0.8}{0.4}\right)^x\left(\frac{0.4}{0.2}\right)^y$

since no constant B, set up 2 trials & divide.

$2 = 2(2)^x \quad 2^x = 1 \quad x = 0$

$R = K[A]^0[B]^1$ or $R = K[B]^1$

b. Calculate the specific rate constant, k. Specify the units for k.

$K = \frac{R}{[B]^1} = \frac{8.0\times10^{-4}\ \frac{mol}{L\cdot s}}{0.20\ \frac{mol}{L}} = 0.0040\ \frac{1}{s}$

c. Calculate the rate of formation of C in trial IV after [A] has decreased to 0.30 M.

Rate = $2.4\times10^{-3}\ \frac{mol}{L\cdot s}$ since reaction is 0th order in A

d. Calculate the initial concentration of reactant B in trial V.

$[B]^1 = \frac{R}{K} = \frac{4\times10^{-4}\ \frac{mol}{L\cdot s}}{0.0040\ \frac{1}{s}} = 0.10\ M$

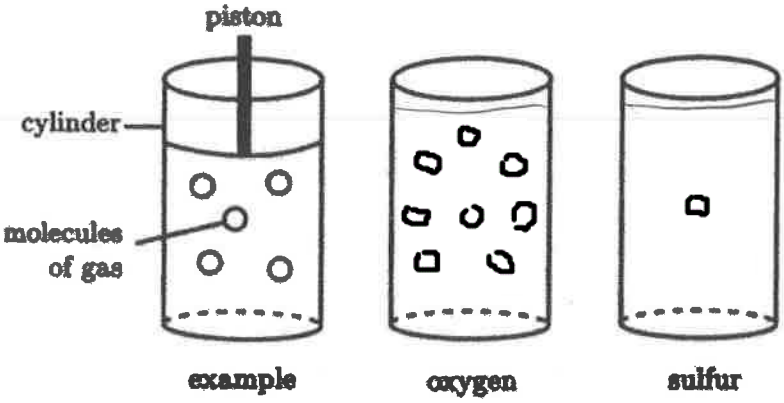
e. If the temperature were raised by 10°C for any trial, what would be the effect on the initial rate of formation for C? Explain.

Initial Rate would increase. In general, an increase of 10°C ~ doubles reaction rate for many reactions since...

$k = Ae^{-\frac{E_a}{RT}}$ bigger T = smaller neg. exponent or more + exponent = greater k.

7. Use principles of the Kinetic Molecular Theory to respond to the questions below.

a. In the space below, complete the sketches of two pistons to represent samples containing 1.60 g of the gas specified in 0.5 liters at 298 K. Each piston should be similar to the example shown.



$\frac{1.60\text{ g } O_2}{32\frac{g}{mol}} = 0.05\text{ mol}$

$\frac{1.60\text{ g } S_8}{256\frac{g}{mol}} = 0.00625\text{ mol}$

$\frac{O_2}{S_8} = \frac{8}{1}$

b. Compare the average kinetic energy of each sample. Explain.

SAME T → same avg. KE

c. Compare the average molecular velocity for each sample. Explain.

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

Since both have the same avg KE, O2 molecules have a higher velocity due to their lower molar mass.

d. Compare the pressure for each sample. Explain.

$PV = nRT$

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

At the same temperature and volume, since their are more moles of O2 gas, the pressure in the oxygen piston will be higher.

8. Using principles of chemical bonding and/or intermolecular forces, explain each of the following.

a. The normal boiling point of iodine, I_2, is greater than the normal boiling point of chlorine, Cl_2.

Both have only dispersion IMF
I_2 → greater molar mass → more electrons → more polarizable → greater dispersion
STRONGER IMF = HIGHER NBP.

b. Both Ag $_{(s)}$ and molten Ag are excellent conductors of electricity. However, silver nitrate, $AgNO_3$, is a good conductor only when melted or dissolved in water. As a solid, it is a poor conductor of electricity.

Ag → metallic bonding → sea of mobile electrons can carry electricity in solid state.
$AgNO_3$ → Ionic bonding → ions in solid in fixed position melt/dissolve → ions free to move & carry electricity.

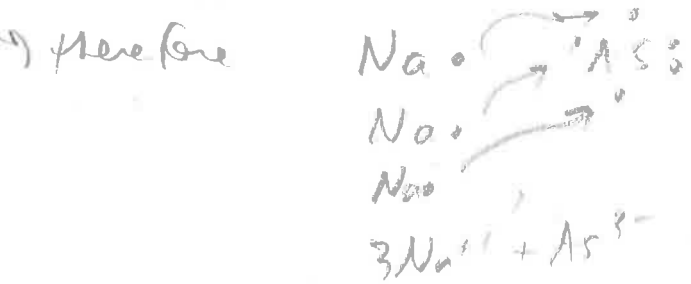
c. The normal boiling point of H_2O is higher than the normal boiling point of H_2S even though the molar mass of H_2O is less than the molar mass of H_2S.

H_2O → dispersion, dipole, H-bonding
H_2S → dispersion, dipole
while H_2S has greater dispersion, H_2O has hydrogen bonds which are stronger.

d. Arsenic, As, reacts with the metal sodium, Na, to form Na_3As. Arsenic reacts with the nonmetal chlorine, Cl_2, to form $AsCl_3$.

Sodium has a lower IE than As, As great E.A.
As has greater electronegativity than Na. As IE > Cl
Cl has greater electronegativity than As. Cl EA > As

therefore



$3Na^+ + As^{3-} \rightarrow Na_3As$

$As^{+3} + 3Cl^- \rightarrow AsCl_3$