KEY

AP CHEMISTRY PRACTICE Unit 1

1. A student is given 50.0 mL of a solution of Na_2CO_3 of unknown concentration. To determine the concentration of the solution, the student mixes the solution with excess 1.0 M $Ca(NO_3)_2$ (aq), causing a precipitate to form. The balanced equation for the reaction is shown below

$$Na_2CO_3(aq) + Ca(NO_3)_2(aq) \rightarrow 2\ NaNO_3\ (aq) + CaCO_3(s)$$

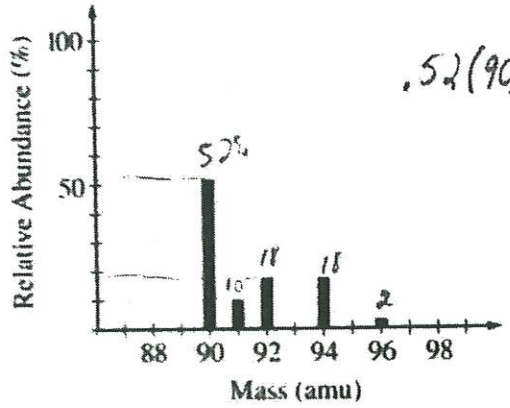
The student filters and dries the precipitate of $CaCO_3$ (molar mass 100.1 g/mol) and records the data in the table below.

Volume of Na_2CO_3 solution	50.0 mL
Volume of 1.0 M $Ca(NO_3)_2$ added	100.0 mL
Mass of $CaCO_3$ precipitate collected	0.93 g

Determine the number of moles of Na_2CO_3 in the original 50.0 mL of solution.

$.93\,g\,CaCO_3 \,/\, 100.1\,g\,CaCO_3 = .0093\,mol\,CaCO_3 \,/\, 1\,mol\,CaCO_3 = .0093\,mol\,Na_2CO_3$

2. The mass spectrum of element X is presented in the diagram below. Based on the spectrum, what is the identity of element X?



$.52(90) + .10(91) + .18(92) + .18(94) + .02(96) = 91.2$

1.2 Mass Spectroscopy of Elements FRQ

3. The average atomic mass of naturally occurring neon is 20.18 amu. There are two common isotopes of naturally occurring neon as indicated in the table below

Isotope	Mass (amu)
Ne-20	19.99
Ne-22	21.99

90.5%
9.5%

(i) Using the information above, calculate the percent abundance of each isotope.

$20.18 = X(19.99) + 1-X(21.99)$

$20.18 = 19.99X + 21.99 - 21.99X$

$-1.81 = -2X$

$X = .905$

1.3 Elemental Composition of Pure Substances FRQ

4. A 31 g sample of a compound that contains only the elements C, H and N is completely burned in O_2 to produce 44.0 g of CO_2, 45.0 g of H_2O, and 92.0 g of NO_2. Determine the empirical formula of the compound.

$44.0\ g\ CO_2 \times \frac{1\ mol}{44\ g} = 1\ mol\ C$ | $45.0\ g\ H_2O \times \frac{1\ mol}{18.0\ g} = 2.5\ mol\ H_2O \times \frac{2\ H}{1\ H_2O} = 5\ mol\ H$ | $92.0\ g\ NO_2 \times \frac{1\ mol}{46.5\ g} = 2\ mol$

$1\ mol\ CO_2 : 1\ mol\ C$ | $C_1H_5N_2$ | $\boxed{CH_5N_2}$ | $\frac{2\ mol\ NO_2}{1\ mol\ NO_2} = \frac{2\ mol\ N}{1\ mol\ N}$

1.4 Composition of Mixtures

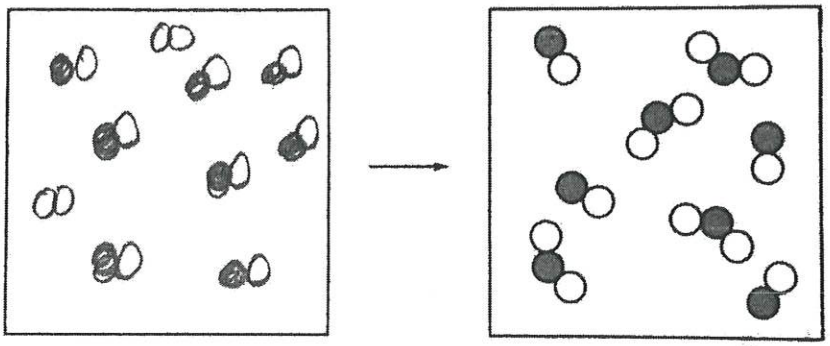
$$2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$$

5. A student investigates the reactions of nitrogen oxides. One of the reactions in the investigation requires an equimolar mixture of NO(g) and $NO_2(g)$, which the student produces by using the reaction represented above.

(a) The particle-level representation of the equimolar mixture of NO(g) and $NO_2(g)$ in the flask at the completion of the reaction between NO(g) and $O_2(g)$ is shown below in the box on the right. In the box below on the left, draw the particle-level representation of the reactant mixture NO(g) and $O_2(g)$ that would yield the product mixture shown in the box on the right. In your drawing, represent oxygen atoms and nitrogen atoms as indicated below.

Law conservation of mass means = # N O R + P

Oxygen atom = ○ Nitrogen atom = ●

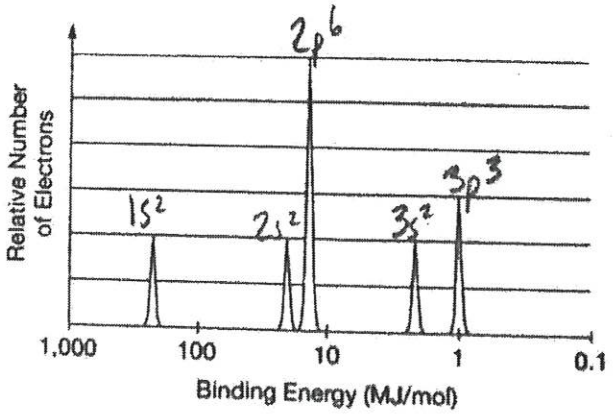


8 N
12 O

Reactant Mixture | Product Mixture

1.6 Photoelectron Spectroscopy

6. The complete photoelectron spectrum of an element is given above. What is the electron configuration of the element with this spectrum?



15 e⁻ = P

1.7 Periodic Trends

7. The elements in which of the following have most nearly the same atomic radius?

(A) Be, B, C, N
B. Ne, Ar, Kr, Xe X
C. Mg, Ca, Sr, Ba X
D. C, P, Se, I X
E. Cr, Mn, Fe, Co

8. Using the following elements from the periodic table, select which one that best fits each statement:

A. Se
B. Br
C. Ag
D. Cs
E. Pb

1. Has the highest electronegativity B
2. Has the largest atomic radius D
3. Has the lowest first-ionization energy D

1.8 Valence Electrons and Ionic Compounds

9. Atoms of Mg combine with atoms of F to form a compound. Identify another element that you would expect to combine with atoms of F in the same ratio?

Be, Ca, Sr, Ba or Ra

10. The only common oxide of zinc has the formula ZnO

(i) Write the electron configuration for a Zn atom in the ground state. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$

(ii) From which sublevel are electrons removed when a Zn atom in the ground state is oxidized? 4s

11. Answer the following questions related to Fe and its ions, Fe^{2+} and Fe^{3+}.

(a) Write the ground-state electron configuration of the Fe^{2+} ion.

Ion	Ionic Radius (pm)
Fe^{2+}	92
Fe^{3+}	79

$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$

(b) The radii of the ions are given in the table above. Using the principles of atomic structure, explain why the radius of the Fe^{2+} ion is larger than the radius of the Fe^{3+} ion.

Fe^{3+} has larger charge so attraction is more in cmpd
or both Fe^{2+} + Fe^{3+} same # energy levels but Fe^{3+} has less e so less e⁻ rpulsn

(c) Fe^{3+} ions interact more strongly with water molecules in aqueous solution than Fe^{2+} ions do. Give one reason for this stronger attraction, and justify your answer using Coulomb's law.

Fe^{3+} ← higher charge so Coulombs law $\frac{Q_1 Q_2}{r}$ is larger and also r is smaller so interaction is stronger

Fe^{2+}

KEY

AP CHEMISTRY PRACTICE
Unit 2

2.1 Types of Chemical Bonds

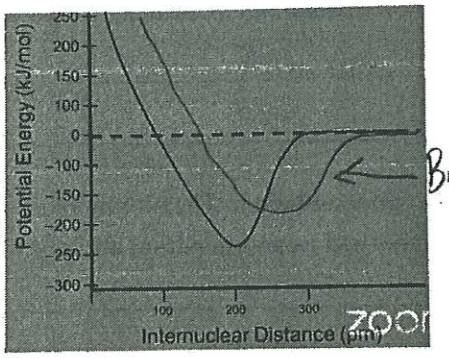
Diagram of Potential Energy versus Internuclear Distance

1. Consider the following information for the Cl—Cl bond:

Bond	Cl—Cl	Br—Br
Bond Length (pm)	200	? ↑
Bond Energy (kJ/mol)	243	? ↓

Br larger than Cl

Make a prediction about the Br—Br bond, in terms of bond length and bond energy. Draw on the graph below the Br-Br bond



Br-Br

2. Data for the lattice energy of NaF is given in the table below. Make predictions about the lattice energy of MgO and KCl. Do you predict that the lattice energy of each compound is less than 930 kJ/mol or greater than 930 kJ/mol? Justify your answer in terms of periodic properties and Coulomb's law.

$\frac{Q_1 Q_2}{r}$

Reaction	Lattice Energy (kJ/mol)
$NaF(s) \rightarrow Na^+(g) + F^-(g)$	930
$MgO(s) \rightarrow Mg^{2+}(g) + O^{2-}(g)$	greater than 930
$KCl(s) \rightarrow K^+(g) + Cl^-(g)$	less than 930

+2 -2
same charge
K + Cl both larger than Na + F
So r is larger
So Energy is small

Metallic so mobile e- to carry charge

Solid	Does the solid conduct electricity?
Cu(*s*)	yes
$CuCl_2(g)$	no

ionic bond e- are locked in are can't conduct

3. A student checked the conductivity of two different solids, and the results are listed in the table above.
Explain why the student got these results, in terms of principles of chemical bonding. Your explanation should include a discussion of the specific particles present in each substance and how the behavior of these particles is related to the conductivity of the solid.

Element	Atomic radius (pm)
Cu	130
Zn	125

Brass is an alloy that contains copper and zinc. The atomic radii of the elements are given in the table above. Should brass be classified as an interstitial alloy or a substitutional alloy? Justify your answer.

similar atomic radius

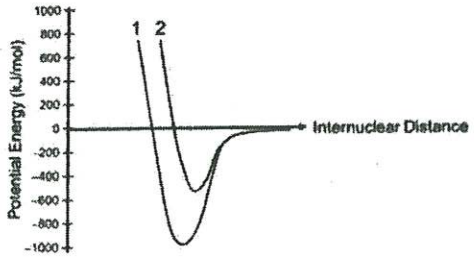
Element	Atomic radius (pm)
Fe	132
C	76

Steel is an alloy that contains iron and carbon. The atomic radii of the elements are given in the table above. Should steel be classified as an interstitial alloy or a substitutional alloy? Justify your answer.

different atomic radius

4. Answer the following questions about nitrogen and oxygen.

(a) Write the Lewis electron-dot structure for the diatomic molecules N_2 and O_2.



(b) The potential energy as a function of internuclear distance for the diatomic molecules N_2 and O_2 is shown in the graph above. Based on the data in the graph and the Lewis structures that you drew in part (a), which curve, 1 or 2, is the better representation of the N_2 molecule? Justify your answer in terms of the principles of chemical bonding and bond energy. :N≡N: has shorter + stronger bond as ≡ bond stronger than O=O

5. Answer the following questions related to Mg and Sr.

(a) Write the complete ground state electron configuration for the ions Mg^{2+} and Sr^{2+}.

$1s^2 2s^2 2p^6 = Mg^{2+}$

$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 = Sr^{2+}$

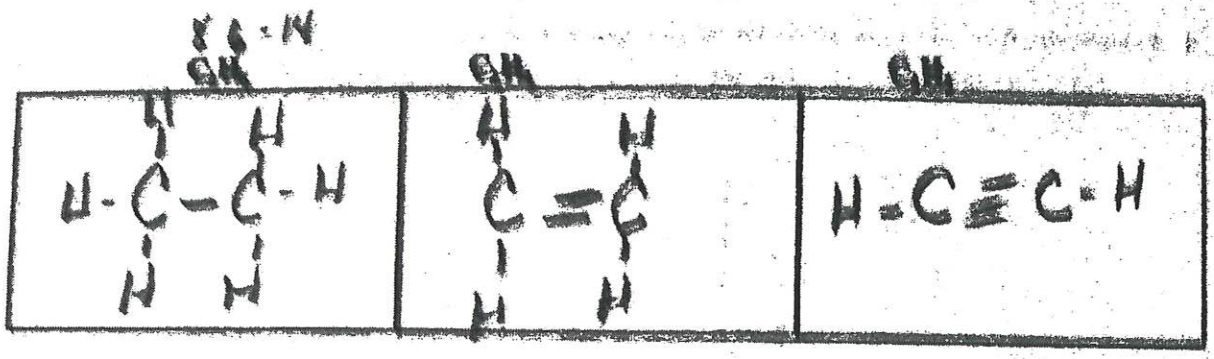
(b) Do you predict that the ionic radius of Sr^{2+} is larger or smaller in size than the ionic radius of Mg^{2+}? Justify your answer in terms of atomic structure and the electron configuration of each ion. Sr^{2+} is larger as it has more energy levels so more e⁻e repulsion + distance between nuclear charge

(c) The lattice energy of $MgCl_2(s)$ is equal to 2300 kJ/mol. Do you predict that the lattice energy of $SrCl_2$ should be less than or greater than 2300 kJ/mol? Justify your answer in terms of Coulomb's law. as the r is larger so LE will be smaller

Drawing Lewis Electron Dot Diagrams (Structures)

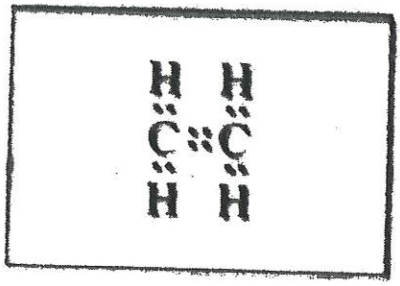
6.

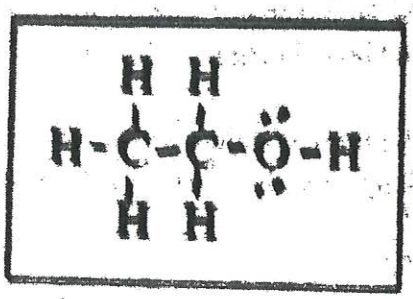
CH_4	NH_3	H_2O	CH_2Cl_2
H-C-H (H)	H-N-H (H)	H-O (H)	Cl-C-H (Cl, Cl, H)



7. Example AP Question

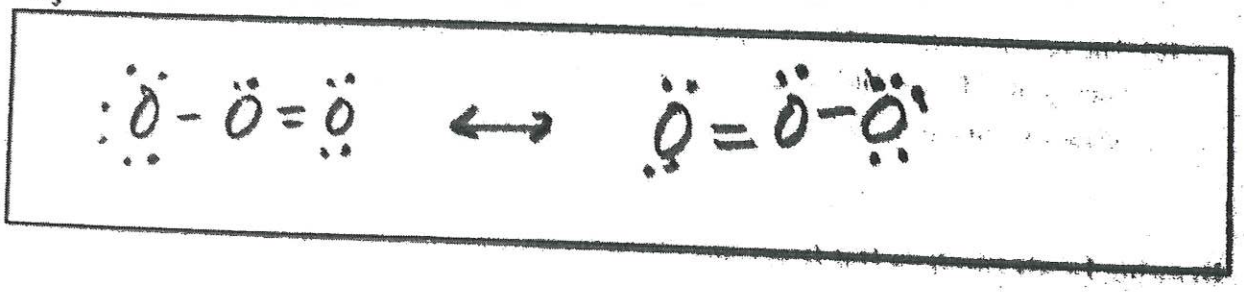
(d) The Lewis electron-dot diagram for C_2H_6 is shown below in the box on the left. In the box on the right, complete the Lewis electron-dot diagram for C_2H_5OH by drawing in all of the electron pairs.





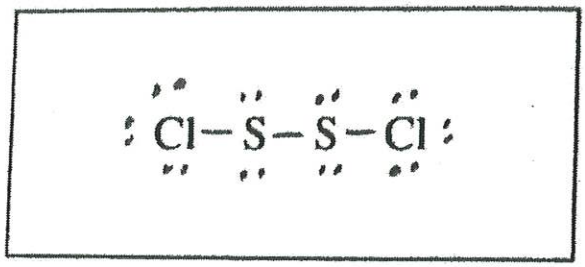
8. Resonance Structures - more than one equivalent Lewis structure can be drawn for a molecule or polyatomic ion

O_3



12. S_2Cl_2 is a product of a reaction.

(i) In the box below, complete the Lewis electron-dot diagram for the S_2Cl_2 molecule by drawing in all of the electron pairs.

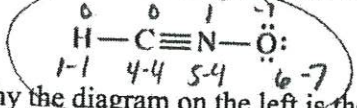


12
14
26

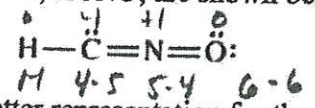
(ii) What is the approximate value of the Cl—S—S bond angle in the S_2Cl_2 molecule that you drew in part (c)(i) ? (If the two Cl—S—S bond angles are not equal, include both angles.) Bent 107.9

13. Answer the following questions about the isomers fulminic acid and isocyanic acid.

Two possible Lewis electron-dot diagrams for fulminic, HCNO, are shown below.



0 0 1 -1
H—C≡N—Ö:
1-1 4-4 5-4 6-7



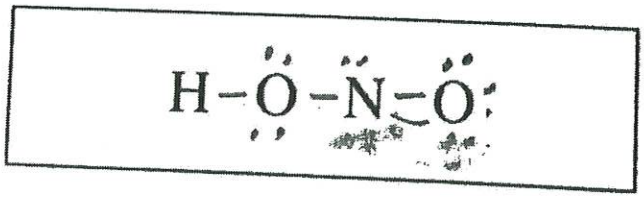
0 -1 +1 0
H—C=N=Ö:
1 4-5 5-4 6-6

(a) Explain why the diagram on the left is the better representation for the bonding in fulminic acid. Justify your choice based on formal charges.

-1 is on more electronegative element O than C

14. (d) The skeletal structure of the HNO_2 molecule is shown in the box below.

(i) Complete the Lewis electron-dot diagram of the HNO_2 molecule in the box below, including any lone pairs of electrons. 1+5+12 = 18



(ii) Based on your completed diagram above, identify the hybridization of the nitrogen atom in the HNO_2 molecule.

Sp²

Unit 3 KEY

1) heating breaks the intermolecular forces

2) #2 has stronger forces b/c BP is higher so takes more energy to break forces. + boil substance

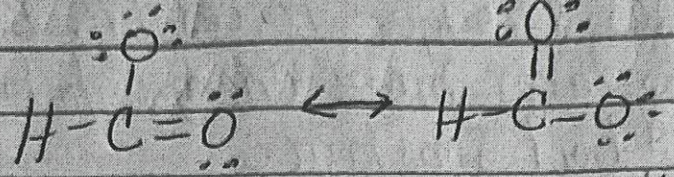
3) i H-Cl LDF and dipole-dipole forces
   ii CCl_4 has stronger forces as it has higher BP b/c it condenses @ higher temp.

4) C_5H_{12} b/c it has lower BP so it will have been creating vapor longer so higher vapor pressure

5) a) Both pentane and propane are nonpolar and only have LDF. Pentane is larger substance with more electrons so it is more polarizable and in turn creates stronger LDF so would remain liquid longer

b) propane is a nonpolar molecule that has LDF only whereas methanol is a polar molecule with LDF and hydrogen bonding. Methanol has stronger forces so remains a liquid

c) methanol sp^3
methanoic ac sp^2

d) i) 

electrons are shared equally between b/c of the resonance.

ii) methanol has single bonds C-O
methanoate has 1 single + 1 double
methanal has 1 double

6) $1.15\,atm \left(\frac{.010}{(.010+.015+.025)}\right) = .23\,atm\ H_2$

$1.15\,atm \left(\frac{.015}{.010+.015+.025}\right) = .35\,atm\ O_2$

$1.15 - (.23+.35) = .57\,atm\ N_2$

7) 1) Ar has larger radius takes up more volume ideal gases take less volume so Ne is more like ideal gas

2) CH_4 is nonpolar whereas NH_3 is polar CH_4 has only LDF; NH_3 has LDF and Hydrogen bonding. NH_3 stronger forces are more attracted to each other so less collisions w/ side + less pressure

8) a) $.0360\,g\,Mg \left| \frac{1\,mol\,Mg}{24.3\,g} \right. = .00148\,mol\,Mg$

b) $.00148\,mol\,Mg \left| \frac{2\,H^+}{1\,Mg} \right| \frac{6.02\times10^{23}\,molec}{1\,mole\,H^+} = 8.92\times10^{20}\,\frac{molec}{H^+}$

c) $749\,torr - 21\,torr = 728\,torr \left| \frac{1\,atm}{760\,torr} \right. = .958\,atm$

d) $PV = nRT$

$(.958\,atm)(V) = (.00148\,mol)(.08206\,\frac{L\,atm}{mol\,K})(296\,K)$

$V = .0375\,L$

9) a) $56\,g\,SrI_2 \left| \frac{1\,mol}{341.43\,g} \right| \frac{2\,I^-}{1\,SrI_2} = .32\,mol\,I^- = .2\,M$
$1.65\,L$

b) $0.100\,M = \frac{X\,mol}{.245\,L} = .0245\,mol\,Na_3PO_4 \left| \frac{3\,Na^+}{1\,Na_3PO_4} \right. = .0735\,\frac{mol}{Na^+}$

c) $.175\,M\,CuSO_4 \cdot 5H_2O = \frac{X\,mol}{.250\,L} = .04375\,mol\,CuSO_4 \cdot 5H_2O$

$.0438\,mol\,CuSO_4 \left| \frac{249.68\,g}{1\,mol} \right. = 10.9\,g$

10) $0.10\,M\,NO_3^- \left| \frac{1\,Al(NO_3)_3}{3\,NO_3^-} \right| \frac{1\,Al^{3+}}{1\,Al(NO_3)_3} = .033\,M\,Al^{3+}$

11) ~28-44 mL higher BP relates to stronger forces

12) I_2 is nonpolar has LDF only
H_2O is polar has hydrogen bonding
C_6H_{14} is nonpolar has LDF only
Like dissolves like so polar/polar + nonpolar/nonpolar so I_2 dissolves in C_6H_{14}

13) b b/c both are polar molecules

14) ~4×10^{-5} M

moles Fe^{3+} $4 \times 10^{-5} M = \frac{x}{.125L}$ $= 5 \times 10^{-6}$ moles Fe^{3+} sent –

5×10^{-6} m.b Fe^{3+}

15) the dilution wont be correct there could be water in the cuvette so decrease the concentration

Unit (4) Key

1) $Ca(OH)_2(s) + 2HBr(aq) \rightarrow H_2O(\ell) + CaBr_2(aq)$

2) $3Mg(NO_3)_2(aq) + 2Na_3PO_4(aq) \rightarrow 6NaNO_3(aq) + Mg_3(PO_4)_2(s)$

3) $CaCl_2(aq) \rightarrow Ca^{2+}(aq) + 2Cl^-(aq)$

4) $H_3PO_4(aq) + 3KOH \rightarrow 3H_2O(\ell) + K_3PO_4(aq)$

$3H^+_{(aq)} + PO_4^{3-}{}_{(aq)} + 3K^+_{(aq)} + 3OH^-_{(aq)} \rightarrow 3H_2O(\ell) + 3K^+_{(aq)} + PO_4^{3-}{}_{(aq)}$

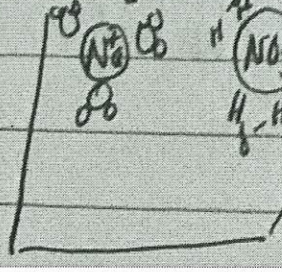
$3H^+_{(aq)} + 3OH^-_{(aq)} \rightarrow 3H_2O(\ell)$

5) 1ST Student
disagree b/c if based on diagram there are 10 Ag^+ in 1.0L in X & 5 Mg in 1.0L in Y they are not same concentration actually $AgNO_3 = 2x\ MgCl_2$

2nd Student
agree b/c both have 5 moles Mg^{2+} but Beaker Y has half the volume as beaker Z so [ ] will be twice.

6) $Na_2CO_3(aq) + Ca(NO_3)_2(aq) \rightarrow CaCO_3(s) + 2NaNO_3(aq)$

a) $CO_3^{2-}{}_{(aq)} + Ca^{2+}_{(aq)} \rightarrow CaCO_3(s)$

b) 

add H_2O surrounding the ions oriented so $-^O$ end toward Na^+ & $+$ H end toward NO_3^-

7) a) $2KI + Pb(NO_3)_2 \rightarrow PbI_2(s) + 2KNO_3$

i $2I^-_{(aq)} + Pb^{2+}_{(aq)} \rightarrow PbI_2(s)$

ii shows substances that are involved in reaction eliminates spectator ions that do not participate in creating ppt.

b) to make sure filter paper is completely dry so H_2O does not affect results

c) $[K^+] < [NO_3^-]$ b/c $Pb(NO_3)_2$ is added in excess

d $1.698g - 1.462g = .238g\ PbI_2 \left| \frac{1mol\ PbI_2}{461g\ PbI_2} \right. = 5.1200 \times 10^{-4}\ mol$

e $5.12 \times 10^{-4} mol\ PbI_2 \left| \frac{2I^-}{1\ PbI_2} \right| \frac{126.9g\ I^-}{1mol\ I^-} = .130g\ I^-$ ~~x100~~

$\frac{.130g}{.425g} = 30.6\%$

f. same as all the I was removed, the water does not affect the results

8) $2Al(s) + 6HCl \rightarrow 2AlCl_3 + 3H_2$

Mole to Mole $.036\ mol\ AlCl_3 \left| \frac{3H_2}{2AlCl_3} \right. = .054\ mol\ H_2$

Grams to Grams $75g\ H_2 \left| \frac{1mol\ H_2}{2.0g\ H_2} \right| \frac{2Al}{3H_2} \left| \frac{26.98g\ Al}{1mol\ Al} \right. = 674.5g\ Al$

Connect to Molar $\frac{4.25\text{g Al}}{26.98\text{g Al}} \left| \frac{1\text{mol Al}}{2\text{Al}} \right| \frac{6\text{HCl}}{2\text{Al}} = \frac{.473\text{mol HCl}}{x\text{ L}} = 5.0\text{M}$

$.0945\text{L}$

Connect to ideal gas

$\frac{35\text{g Al}}{26.98\text{g Al}} \left| \frac{1\text{mol Al}}{2\text{Al}} \right| \frac{3\text{H}_2}{2\text{Al}} = 1.95\text{mol H}_2$

$PV = nRT \qquad 1.12\text{atm}(V) = 1.95\text{mol}\left(.08206 \frac{\text{L·atm}}{\text{mK}}\right)(345\text{K})$

$V = 49.29\text{L}$

LR + TY

$\frac{125\text{g Al}}{26.98\text{g Al}} \left| \frac{1\text{mol Al}}{2\text{Al}} \right| \frac{3\text{H}_2}{2\text{Al}} \left| \frac{2.0\text{g H}_2}{1\text{mol H}_2} \right. = 13.9\text{g H}_2$

$3.20\text{M} = \frac{x}{2.50\text{L}} = \frac{8\text{mol HCl}}{6\text{HCl}} \left| \frac{3\text{H}_2}{1\text{H}_2} \right| \frac{2.0\text{g H}_2}{1\text{H}_2} = 8.0\text{g H}_2$

A HCl is LR $\qquad 8.0\text{g H}_2 = \text{TY}$.

9. $(.025\text{L})(M_A) = .03204\text{L}(.650\text{M})$

$M_A V_A = M_B V_B \qquad M_A = .833\text{M}$

10)

CA	CB
HF	F^-
NH_4^+	NH_3
$HC_2H_3O_2$	$C_2H_3O_2^-$
HSO_4^-	SO_4^{2-}

11) 3rd one only

$Zn + 2HCl \rightarrow ZnCl_2 + H_2$ = REDOX

$AgNO_3 + HCl \rightarrow AgCl(s) + HNO_3$ = ppt

$Ba(OH)_2 + 2HCl \rightarrow BaCl_2 + H_2O$ = A/B bc $A + B \rightarrow$ salt + H_2O

12) $\overset{+2\ -2}{FeS} + \overset{+1\ +5\ -2}{HNO_3} \rightarrow \overset{+2\ +5\ -2}{Fe(NO_3)_2} + \overset{+1\ -2}{2H_2O}$

NO All oxidation # remain the same in order to be be a REDOX there has to be a change in oxidation state

$1e + Fe^{3+} \rightarrow Fe^{2+}$

$Sn^{2+} \rightarrow Sn^{4+} + 2e$

~~$\overset{+1\ -2}{HNO_3} + H^+ \rightarrow \overset{+2\ -2}{NO} + \overset{+1\ -2}{2H_2O}$~~

13)

a) $6H^+ + 2\overset{+7\ -2}{MnO_4^-} + 5\overset{+1\ +3\ -2}{H_2C_2O_4} \rightarrow 10\overset{+4\ -2}{CO_2} + 8H_2O + 2\overset{+2}{Mn^{2+}}$

MnO_4^- gain $5e^-$ is reduced

b) $29.6 - 3.4 = 26.20\,mL$

$(.02620L)(.0235M) = 6.16 \times 10^{-4}$ moles

c) $.00143M = \frac{6.16 \times 10^{-4}\,mol}{XL} = 430.6\,mL$

way beyond the 50.0 mL burette capacity

Unit 5 Review KEY

1) $3.5\times10^{-4}\ Br^- \left|\frac{3Br_2}{5Br^-}\right. = 2.1\times10^{-4}\ \frac{mol\ Br_2}{L\,s}$

$3.5\times10^{-4}\ Br^- \left|\frac{6H^+}{5Br^-}\right. = 4.2\times10^{-4}\ \frac{mol\ H^+}{L\,s}$

2) Exp 2 because higher $[H^+]$ so more molecules so more collisions so more effective collisions (remember effective = enough energy + correct orientation) so ↑ rate.

3) Exp 1 powder $CaCO_3$ will have more surface area so more exposed molecules so more collisions so more effective collisions so ↑ rate

4) Exp 2 higher temp means molecules are moving faster so ↑ # collisions so ↑ effective collisions so ↑ rate.

5) for $[NO]$ use trial 3 + 4 $[NO]$ doubles rate doubles so order for NO = 1

for $[O_3]$ use trial 1 + 2 $[O_3]$ doubles rate doubles so order for O_3 = 1

$$\text{rate} = k[NO][O_3]$$

$$6.60\times10^{-5}\ \frac{mol}{L\cdot s} = k\left(1\times10^{-6}\ \frac{mol}{L}\right)\left(3.0\times10^{-7}\ \frac{mol}{L}\right) \qquad \frac{mol^2}{L^2}$$

$$k = 2.20\times10^{7}\ mol^{-1}\,s^{-1}\,L$$

$\frac{mol\ L^2}{mol^2\ L\ s}$

6.) for [NO] use trials 1+2
[NO] doubles rate quadruples
so [NO] order = 2
for $[H_2]$ use trials 2+3
$[H_2]$ doubles + rate doubles
so $[H_2]$ orde = 1
rate = $k[NO]^2[H_2]$

$$\frac{2.835 \times 10^{-3} \text{ mol}}{\text{L} \cdot \text{s}} = k\left(.80 \frac{\text{mol}}{\text{L}}\right)^2\left(.35 \frac{\text{mol}}{\text{L}}\right)$$

$K = .09\ \text{L}^2\text{mol}^{-2}\text{sec}^{-1}$

~~mol~~ L^3
$K\,sec\,mol^{-2}$

7) a) 1ST order, since ln abs graph has straight line
b) increasing conc of food coloring
b/c ↑ [fc] then more time for bleach to oxidize food coloring
c) Use different wavelength on Spectrophotometer

8) rate = $k[HBr][O_2]$

9) rate = $k[NO_2][F_2]$

10) Reactants → ●○ Products → ●●
Intermediates → ●○● Catalysts None

11) Reactants NO ; H_2 Products → H_2O
Intermediate - H_2O_2 Catalysts → None

12) rate $= k[NO]^2[Br_2]$
FYI sometime the intermediate can be in rate law but College board doesn't usually ask this in their tested?

13) a) $1/[NO_2]$ is the straight line so 2nd order
b) rate $= k[NO_2]^2$
c) i) yes rds = step 1 so rate $= k[NO_2]^2$
ii) yes intermediates cancel + combine step 1 + 2
rate $= k[NO_2]^2$

14) Diagram 1 + 2
Diagram 1 is the catalyzed one since the activation energy is lower.

15) Diagram 1 = E_a = ~25 kJ
Diagram 2 = E_a = 14 kJ ← Catalyzed

16) Diagram 1
E_a = 80 kJ
← same 2nd step.

Diagram 2
E_a = 70 kJ
Catalyzed →

Disagree

17) Adding a catalyst lowers the activation energy so rxn proceeds faster

18) a) i) $PV = nRT$ $\quad T = 120 + 273$

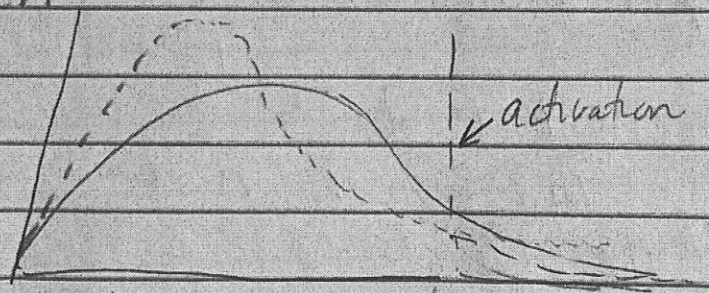
$(0.40 atm)(25.0 L) = n(.08206 \frac{L \cdot atm}{mol \cdot K})(393 K)$

$n = .31$ moles Cl_2

ii) $\frac{.31 mol\ Cl_2}{} \left| \frac{1\ CS_2}{3\ Cl_2} \right| \frac{1 mol\ CS_2}{} \left| \frac{76 g\ CS_2}{} \right. = 7.9 g\ CS_2$

b) i) Molecules are moving faster and are then colliding more often so in turn there are more effective collisions so increased rate of rxn

ii)

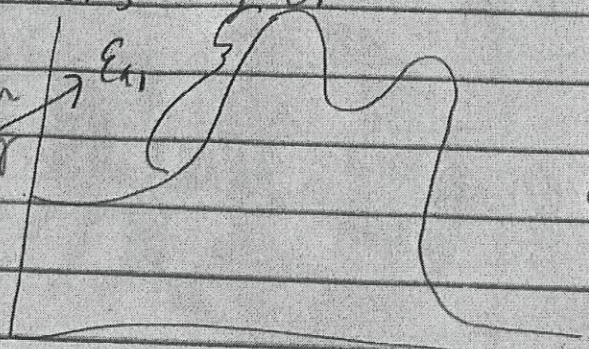


dotted line peaks above + to the left of curve + below the line beyond activation energy

c) rate $= k[C_2H_4][HCl]$

d) $C_2H_5^+$; Cl^-

e)



Unit 6 KEY

1) 1) Endothermic
2) system
3) surroundings to system

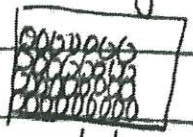
2) a) equal because energy lost by metal = energy gained by water

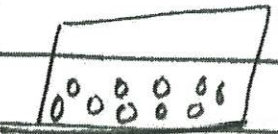
3a) Cu will reach higher temp because the specific heat is smaller so will take less energy to raise temp of Cu compared to H_2O.

4) Segment S is vaporizing where as Q is melting. Vaporizing ($\ell \rightarrow g$) take more energy to break the intermolecular forces to become gas than to become a liquid.

5) CH_4 is a non polar molecule so has LDF only forces
H_2O is a polar molecule so has LDF + hydrogen bonds which are stronger so more energy required to break

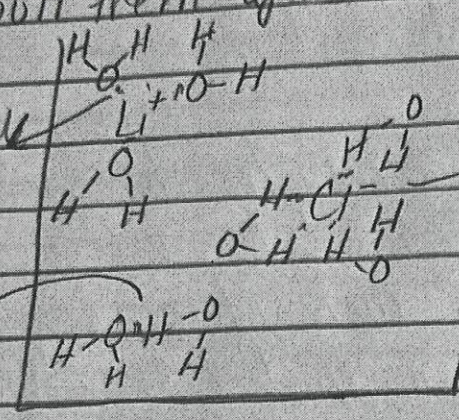
6) a) from surrounding to the wax b/c it is absorbing energy to break forces to melt

b) 
solid


melted

particles have space between them so less particles in same area so less dense

7) H_2O is attracted to the ions in LiCl and pull them apart the H_2O orientates to the ions



8) released $-\Delta H$ = exothermic

1 mol CH_4 = 16g

9) $\frac{7.50\text{g } CH_4}{16\text{g } CH_4} \left| \frac{-802}{} \right. = -376\text{ KJ}$

10) b) bonds broken − bond formed

$[C-H + C\equiv N + N-O] - [H-N + N=C + C=O]$

$[413 + 891 + 201] - [391 + 615 + 745]$

$1505 - 1751 = -246\text{ KJ}$

11) $\Delta H_{prod} - \Delta H_{react}$

$[-393.5 + 2(-241.8)] - [-74.8 + 0]$

$-877.1 - [-74.8] = -802.3\text{ KJ}$

12) c) $Na_2S_2O_3 + \underbrace{4NaOCl}_{LR} + 2NaOH \rightarrow 2Na_2SO_4 + 4NaCl + H_2O$

$\frac{.5}{1} = \frac{X}{.005}$ $\quad \frac{.5}{4} = \frac{X}{.005}$ $\quad \frac{.5}{2} = \frac{X}{.005}$

$.0025$ $\quad .0025$ $\quad .0025$

$\frac{2}{2} = .0025$

$\frac{2}{1} = .005$

$\frac{2}{4} = .00125$

d) $32.5 - 20.0 = 12.5\,^{\circ}C$

Unit 7 Review KEY

$\frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{[1.00][1.00]^3}{[.20]^2} = \frac{1.00}{.04} = 25$

$Q > K$ rxn will shift toward reactants so Prod ↓ react ↑ + Q will ↓ to = K

$25 > 17$

i) $Q = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{(2.0)(1.0)^3}{(3.0)^2} \quad \frac{2.0}{9} = .222$

$Q < K$ rxn will shift toward products so prods ↑ react ↓ + Q will ↑ to = K

$.222 < 6.8 \times 10^4$

2) a) $K = \frac{[C]^2}{[A]^2[B]} = \frac{(.0020)^2}{(.018)^2(.014)} = .88$

b) If K is larger when temperature is raised then the concentrations of the products will increase and concentration of reactants will decrease

3) a) $K = \frac{[CO_2]}{[CH_4][O_2]^2}$ * H_2O is excluded b/c it is a (l)

b) $K = [NO_2]^4[O_2]$ * $Pb(NO_3)_2$ & PbO excluded b/c they are solids

c) $K_b = \frac{[C_8H_{10}NH_2^+][OH^-]}{[C_8H_{10}NO_2]}$ * H_2O is excluded b/c it is a liquid

d) $K_{sp} = [Al^{3+}][NO_3^-]^3$ $Al(NO_3)_3$ excluded b/c it is a solid

4) BrCl will be large b/c K_{eq} is $>>>1$ so rxn favors product

NO will be small b/c $K_{eq} <<<1$ so rxn favors reactants

5) @ equilibrium the rate of reactant & product are equal but the concentrations are not equal. The graph supports this as the lines for the [ ] of the reactants and products are staying constant, running parrall to each other but not equal values

6) $K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(.714)^2}{(.1)(.1)} = 51.0$

7)

R	A	+	B	$\rightleftharpoons$	$2C$
i	.300		.300		0
Δ	$-x$		$+x$		$+2x$
e	$.300-x$		$.300-x$		$0+2x$

$K = \frac{[C]^2}{[A][B]}$, 3 sig figs

$9.0\times10^{-8} = \frac{(2x)^2}{(.300)(.300)}$

$[A] = [B] = .300 - 4.5\times10^{-5} = .3M \quad X = 4.5\times10^{-5}$

$[C] = 2x = 2(4.5\times10^{-5}) = 9\times10^{-5}M$

8)

R	HA	$\rightleftharpoons$	H^+	+	A^-
I	.50		0		0
Δ	$-x$		$+x$		$+x$
e	$.50-x$		x		x

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

$2.0\times10^{-5} = \frac{x^2}{.5}$

$x = 3.1\times10^{-3}$

$[HA] = .50 - x = .50 - 3.1\times10^{-3} = .50M$

$[H^+] = [A^-] = x = 3.1\times10^{-3}M$

a. #1 K_{sp} is the largest

b. $AgBr \rightleftharpoons Ag^+ + Br^-$

$K_{sp} = [Ag^+][Br^-]$

$5.4 \times 10^{-13} = [X][X]$

$X = 7.3 \times 10^{-7}\ M$

$AgI \rightleftharpoons Ag^+ + I^-$

$K_{sp} = [Ag^+][I^-]$

$8.5 \times 10^{-17} = (X)(X)$

$X = 9.2 \times 10^{-9}\ M$

II) $Ag_2SO_4 \rightleftharpoons 2Ag^+ + SO_4^{2-}$

.02 .001

$(.02)^2(.001M) = 4 \times 10^{-7} < 1 \times 10^{-5}$

So will shift right & no ppt form

$PbSO_4 \rightleftharpoons Pb + SO_4^{2-}$

.001 .001

$(.001)(.001) = 1 \times 10^{-6} > 1 \times 10^{-8}$

So will shift left & ppt will form

12.) a) shift toward reactants ; replacing lost H_2S

b) shift toward reactants ; 3 moles gas 5 moles gas shift

c) shift toward products ; energy is reactant for endo ; to release

d) shift toward reactants, away from ↑[ ]

e) shift toward reactants ; replace lost CH_4

15 a) toward products to replace energy.
b) toward reactants; +ΔH is endo so replace
c) toward products -ΔH is exo so replace.

KEY

Unit 8 Review

8.1

A B B CA

$CH_3CH_2COOH(aq) + H_2O(l) \rightleftarrows CH_3CH_2COO^-(aq) + H_3O^+(aq)$

1. 2. Propanoic acid, CH_3CH_2COOH, is a carboxylic acid that reacts with water according to the equation above. At 25°C the pH of a 50.0 mL sample of 0.20 M CH_3CH_2COOH is 2.79.

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

2. Four different examples of acid-base reactions are shown below. In each of these reactions, focus on the H_2O. Decide if H_2O is acting as a Brønsted-Lowry acid or as a Brønsted-Lowry base.

- ☐ $H_2O + HCl \longrightarrow H_3O^+ + Cl^-$ Base
- ☐ $H_2O + HCO_3^{-1} \longrightarrow H_2CO_3 + OH^{-1}$ Acid
- ☐ $H_2O + NH_3 \longrightarrow NH_4^+ + OH^{-1}$ Acid
- ☐ $H_2O + HCO_3^{-1} \longrightarrow H_3O^+ + CO_3^{2-}$ Base

energy + $N_2O_4(g) \rightleftarrows 2\,NO_2(g)$ $\Delta H° = +58\ kJ/mol_{rxn}$

3. The chemical equation shown above represents the reversible reaction in which $N_2O_4(g)$ is converted into $NO_2(g)$. The value of the equilibrium constant, K, for this reaction is equal to 0.005 at 25°C..

If the temperature of the reaction vessel is increased from 25°C to 100°C, do you predict that the value of K will decrease, increase, or remain the same? Justify your answer. ↑T endothermic so will shift → $K = \frac{P}{R}$ so K ↑

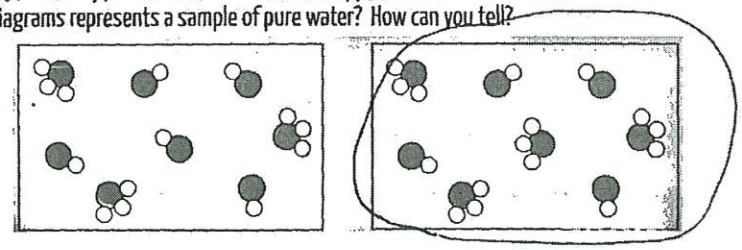
4. A chemist has three different samples of pure water. Each sample is at a different temperature as shown below.

Does each sample have the same pH value? If yes, explain why. If no, explain why not. NO As T changes K changes b/c rxn shifts see previous

If these samples do not have the same pH value, arrange them in order from lowest pH to highest pH.

$H_2O \rightleftarrows H^+ + OH^-$ endothermic so ↓T ← K so less H^+ ↓ ↑pH.

5. Which of these particle diagrams represents a sample of pure water? How can you tell?



Equal $H_3O^+ = OH^-$

6. Fill in the missing information in the table below. Assume that each solution is at 25°C.

$[H_3O^+]$	pH	$[OH^{-1}]$	pOH
$1.0 \times 10^{-9}\ M$	9	1×10^{-5}	5
1.0×10^{-4}	4.0	1×10^{-10}	10

7.

Temperature (°C)	pK_w K_w
10	14.5 3.2×10^{-15}
25	14.0 1×10^{-14}
30	13.8 1.6×10^{-14}

Look closely at these pK_w values.

What happens to the value of pK_w as the temperature increases? ↓

What happens to the value of K_w as the temperature increases? ↑

AP EXAM PRACTICE FRQ 8.1

8. A solution of HI(*aq*) is added to a solution of methylamine, $CH_3NH_2(aq)$. An acid-base reaction takes place. All of the water is removed by evaporation, producing crystals of the ionic compound methylammonium iodide.

(a) In the reaction described above, methylamine and the methylammonium ion represent a conjugate acid-base pair. $HI + CH_3NH_2 \rightarrow CH_3NH_3^+$

(i) Does the methylamine behave as an acid or as a base in this reaction? Justify your answer.

(ii) Write the chemical formula (including the correct charge) for the methylammonium ion. $CH_3NH_3^+$

$$H_2(g) + I_2(g) \rightleftarrows 2\,HI(g)$$

Temperature (K)	Equilibrium Constant, K
298	790
700	55

T ↑ K ↓ so $\frac{P}{R}$ ↓ so Shift ← so exothermic

9. The reaction represented by the balanced equation shown above is an equilibrium system. The value of the equilibrium constant, K, is determined at two different temperatures. The results are shown in the data table above.

(b) Based on the information shown above, is the forward reaction classified as an endothermic process or as an exothermic process? Justify your answer.

8.2 pH and pOH of Strong Acids and Bases

10. If you are given a 0.0025 *M* HCl solution, what is the pH and pOH? pH = 2.60 pOH = 11.40

11. If you are given a 0.0015 *M* NaOH solution, what is the pH and pOH? pH = 2.83 pOH = 11.17

12. Calculate the pH, $[H_3O^+]$, pOH, and $[OH^-]$ of a 1.25×10^{-5} *M* solution of HBr. [HBr] = [H] since 1:1 so pH = 4.9 pOH = 9.1 $[OH] = 7.9\times10^{-10}$

13. Calculate the pH, $[H_3O^+]$, pOH, and $[OH^-]$ of a 3.85×10^{-4} *M* solution of KOH. [OH] since 1:1 so pOH = 3.41 pH = 10.59 $[H] = 2.57\times10^{-11}$

$$CH_3CH_2COOH(aq) + H_2O(l) \rightleftarrows CH_3CH_2COO^-(aq) + H_3O^+(aq)$$

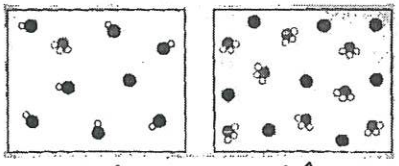
14. Propanoic acid, CH_3CH_2COOH, is a carboxylic acid that reacts with water according to the equation above. At 25°C the pH of a 50.0 mL sample of 0.20 *M* CH_3CH_2COOH is 2.79.

For the following statement, determine whether the statement is true or false. Explain the reasoning that supports your answer.

"If the pH of a hydrochloric acid solution is the same as the pH of a propanoic acid solution, then the molar concentration of the hydrochloric acid solution must be less than the molar concentration of the propanoic acid solution." True HCl is a SA ionizes completely less HCl molecules needed to produce same $[H_3O^+]$ as propanoic

8.3 Weak Acid Base Equilibria

15. Which of the diagrams represents a strong acid, which one represents a weak acid?



WA SA

Relationship between K_a (or pK_a) and Acid Strength

16. $CH_3COOH + H_2O \leftrightarrows H_3O^+ + CH_3COO^-$ $\quad K_a = 1.8 \times 10^{-5}$

$HF + H_2O \leftrightarrows H_3O^+ + F^-$ $\quad K_a = 6.8 \times 10^{-4}$

Two examples of weak monoprotic acids are acetic acid, CH_3COOH, and hydrofluoric acid, HF. There equilibrium dissociations and K_a's are given above. Which of these two weak acids is the stronger acid? How can you tell?

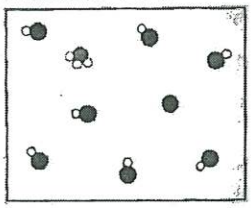
↓ larger Ka

Percent Ionization

17. Based on this particle diagram, what is the percent ionization of this acid?

$\frac{1}{8}$ $8HX \rightleftharpoons 1H_3O^+ + 7X^-$

$= 12.5\%$



8.3 Weak Acid Base Equilibria

18. $CH_3COOH + H_2O \leftrightarrows H_3O^+ + CH_3COO^-$

Acetic acid, CH_3COOH, is a weak monoprotic acid that reacts with water according to the equation shown above. A solution of 0.10 M CH_3COOH has a pH of 2.87. $[H^+] = .00134$

$CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$

	0	0
.10		
$-X$	$+X$	$+X = .00134$
.0986	.00134	.00134

$\frac{(.00134)(.00134)}{.0986} = 1.82 \times 10^{-5} = K_a$

1. Calculate the value of K_a for CH_3COOH.
2. Calculate the percent ionization for 0.10 M CH_3COOH.

$\frac{.00134}{.10} \times 100 = 1.34\%$

19. $HOCl + H_2O \leftrightarrows H_3O^+ + ClO^-$

Hypochlorous acid, HClO, is a weak monoprotic acid that reacts with water according to the equation shown above. The K_a for HOCl is 3.0×10^{-8}.

$HOCl \rightleftharpoons H_3O^+ + ClO^-$

	0	0
.10		
$-X$	$+X$	$+X$
$.10-X$	X	X

$3.0 \times 10^{-8} = \frac{X^2}{.10}$ $\quad X = 5.4 \times 10^{-5}$

1. Calculate the pH of a 0.10 M HOCl. $\quad pH = 4.26 \leftarrow [H_3O^+]$
2. Calculate the percent ionization for 0.10 M HOCl.

$\frac{5.4 \times 10^{-5}}{.1} \times 100 = .054\%$

20.

21. $(CH_3)_3N + H_2O \leftrightarrows (CH_3)_3NH^+ + OH^-$

Trimethylamine, $(CH_3)_3N$, is a weak base that reacts with water according to the equation shown above. The K_b for $(CH_3)_3N$ is 6.4×10^{-5}.

$(CH_3)_3NH_2 + H_2O \rightleftharpoons (CH_3)_3NH^+ + OH^-$

	0	0
.10		
$-X$	$+X$	$+X$
$.10-X$	X	X

$6.4 \times 10^{-5} = \frac{X^2}{.10}$ $\quad X = .0025M = [OH^-]$

1. Calculate the pH of a 0.10 M $(CH_3)_3N$. $\quad pOH = 2.60 \quad pH = 11.4$
2. Calculate the percent ionization of 0.10 M $(CH_3)_3N$.

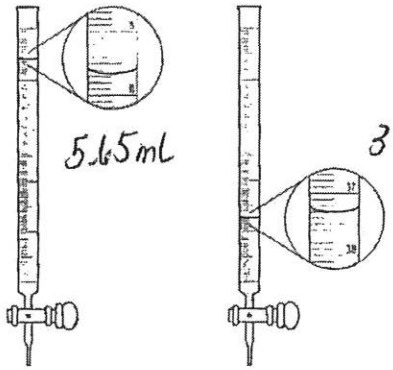
$\frac{.0025}{.10} \times 100 = 2.5\%$

AP STYLE FRQ

22. A student is given a 25.0 mL sample of a solution of an unknown monoprotic acid and asked to determine the concentration of the acid by titration. The student uses a standardized solution of 0.110 M NaOH(aq), a buret, a flask, an appropriate indicator, and other laboratory equipment necessary for the titration.

(a) The images below show the buret before the titration begins (below left) and at the end point (below right). What should the student record as the volume of NaOH(aq) delivered to the flask?

.1 increments so need one more digit that is estimated



37.30mL − 5.65 = 31.65mL

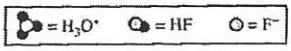
(b) Based on the given information and your answer to part (a), determine the value of the concentration of the acid that should be recorded in the student's lab report. $M_A V_A = M_B V_B$ $M_A(25mL) = .110M(31.7mL)$ $M_A = .14M$

(c) In a second trial, the student accidentally added more NaOH(*aq*) to the flask than was needed to reach the end point, and then recorded the final volume. Would this error increase, decrease, or have no effect on the calculated acid concentration for the second trial? Justify your answer. ↑ V_D so ↑ M_B

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

23. The ionization of HF(*aq*) in water is represented by the equation above. In a 0.0350 *M* HF(*aq*) solution, the percent ionization of HF is 13.0 percent.

(a) Two particulate representations of the ionization of HF molecules in the 0.0350 *M* HF(*aq*) solution are shown below in Figure 1 and Figure 2. Water molecules are not shown. Explain why the representation of the ionization of HF molecules in water in Figure 1 is more accurate than the representation in Figure 2. (The key below identifies the particles in the representations.)



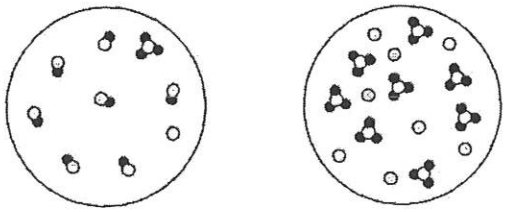


Figure 1 Figure 2

only 13% of the molecular dissociates figure 2 has all of the HF gone so acting like a SA

$\frac{X}{.0350} = .13$ $X = .00455$

(b) Use the percent ionization data above to calculate the value of K_a for HF. $\frac{(.00455)(.00455)}{.0350} = 5.9 \times 10^{-4}$

(c) If 50.0 mL of distilled water is added to 50.0 mL of 0.035 *M* HF(*aq*), will the percent ionization of HF(*aq*) in the solution increase, decrease, or remain the same? Justify your answer with an explanation or calculation. more dilute HF ↑% ionization

8.4 Acid-Base Reactions and Buffers

Identifying Strong versus Weak Acids

24. Which of the following are strong acids? Which of the following are weak acids? Label each as such.

- ☐ HCl, hydrochloric acid — strong
- ☐ HBr, hydrobromic acid — strong
- ☐ $HC_2H_3O_2$, acetic acid — weak
- ☐ HNO_2, nitrous acid — weak
- ☐ HNO_3, nitric acid — strong

Definition of a Buffer and Examples of Buffer Solutions

25. Write in all the conjugate bases of all the conjugate acids in the table below.

Conjugate Acid	Conjugate Base
HCl	Cl^-
HBr	Br^-
HNO_3	NO_3^-
HNO_2	NO_2^-
HOCl	OCl^-
HCN	CN^-
HF	F^-
$HC_2H_3O_2$	$C_2H_3O_2^-$

*For a **buffer, you want a WEA ACID and it's conjugate base.** Cannot use these three (Strong Acids) Not make a good buffer.*

Since these five are wea acids, they WOULD make a good buffer solution.

26. We could find the conjugate bases as sodium salts of the conjugate acids:

1.0 $M HNO_2$ and 1.0 $M NaNO_2$ pH=pKa 3.40
1.0 M HOCl and 1.0 M NaOCl 7.54
1.0 M HCN and 1.0 M NaCN 9.21
1.0 M HF and 1.0 M NaF 3.17
1.0 $M HC_2H_3O_2$ and 1.0 $M NaC_2H_3O_2$ 4.74

Guiding Questions

(1) What is the pH of each of these buffer solutions?

(2) Why do they behave as a good pH buffer solution? How exactly does a buffer work? wA/CB absorb added H^+ & OH^- so results pH change

27. Complete the table by calculating the pK_a and pH of buffer solutions $pK_a = -\log(K_a)$

Buffer Components	K_a of the Weak Acid	pK_a of the Weak Acid	pH of the Buffer Solution
1.0 $M HNO_2$ and 1.0 $M NaNO_2$	4.0×10^{-4}	3.40	3.40
1.0 M HOCl and 1.0 M NaOCl	2.9×10^{-8}	7.54	7.54
1.0 M HCN and 1.0 M NaCN	6.2×10^{-10}	9.21	9.21

Using the Henderson-Hasselbach Equation (or Not)

28. A buffer solution contains 1.2 $M HNO_2$ and 0.80 $M NaNO_2$. What is the pH of this buffer solution? ($K_a = 4.0 \times 10^{-4}$)

Solve using the K_a expression AND the Henderson-Hasselbach Equation

$HNO_2 \rightleftharpoons H^+ + NO_2^-$

	1.2	0	.80
	$-X$	X	$+X$
	$1.2-X$	X	$.80+X$

$4.0\times10^{-4} = \frac{X(.80)}{1.2}$ $X = 6.\times10^{-4} = [H^+]$ $pH = 3.22$

$pH = pKa + \log\frac{B}{A}$

$pH = 3.40 + \log\frac{.80}{1.2} = 3.22$

29. A buffer solution that contains a mixture of $HC_2H_3O_2$ and $NaC_2H_3O_2$ has a pH of 5.00. If $[HC_2H_3O_2] = 2.0\ M$, what is the value of the $[C_2H_3O_2^-]$? (K_a for $HC_2H_3O_2 = 1.8 \times 10^{-5}$) **Solve using the K_a expression AND the Henderson-Hasselbach Equation**

$HC_2H_3O_2 \rightleftharpoons H^+ + C_2H_3O_2^-$

$K = \frac{[H^+][C_2H_3O_2^-]}{[HC_2H_3O_2]}$

$1.8\times10^{-5} = \frac{1\times10^{-5}(x)}{2.0}$

$X = 3.6M$

$5.00 = 4.74 + \log\frac{X}{2.0}$

$.26 = \log\frac{X}{2.0}$

$10^{.26} = \frac{X}{2.0}$

$1.82 = \frac{X}{2.0}$ $X = 3.6M$

30. $pK_a + pK_b = 14$ $K_a K_b = 1 \times 10^{-14}$

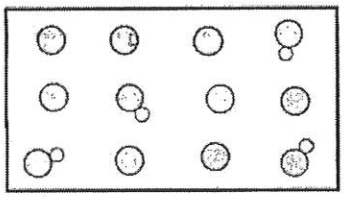
Conjugate Acid	K_a	pK_a	Conjugate Base	K_b	pK_b
HNO_2	4.0×10^{-4}	3.40	NO_2^-	2.5×10^{-11}	10.6
HOCl	2.9×10^{-8}	7.54	ClO^-	3.47×10^{-7}	6.46
NH_4^+	5.5×10^{-10}	9.26	NH_3	1.8×10^{-5}	4.74
$CH_3NH_3^+$	2.29×10^{-11}	10.64	CH_3NH_2	4.4×10^{-4}	3.36

AP EXAM PRACTICE FRQ 8.4, 8.7-8.9

31. Answer the following questions that relates to a buffer solution that contains hydrofluoric acid, HF, and sodium fluoride, NaF. (K_a for HF = 6.8×10^{-4})

(a) The pK_a for HF is equal to 3.17. A diagram shown below is a particulate representation of a buffer solution containing HF and F^-. Based on the information in the diagram, do you predict that the pH of this solution should be less than, equal to, or greater than 3.17? Justify your answer.

4 HF 8F
pH = pKa when HF = F



$pH = pK_a$

$pH = pK_a + \log \frac{B}{A}$

$pH = 3.17 + \log \frac{8}{4} = 3.47$

(b) A buffer solution is made by mixing equimolar amounts of HF(*aq*) and NaF(*aq*). When a small amount of 12 *M* HNO_3(*aq*) is added to this buffer, the pH of the solution changes from 3.17 to 3.15. Write a balanced net ionic equation that accounts for the fact that the pH does not change significantly when the HNO_3(*aq*) is added to the buffer solution. $HF \rightleftharpoons H^+ + F^-$ ↑ H^+ so ←

(c.) Determine the volume, in mL, of 10.0 *M* NaOH(*aq*) that should be added to 1000 mL of 1.0 *M* HF(*aq*) in order to create a buffer solution that has a pH of 3.17. Justify your answer with calculations.

$10 = \frac{.05}{X} = .005L$ 5mL so ½ reacts

$HF + OH^- \rightarrow F^- + H_2O$ X

	1.0	~~.05~~	0
	−.05	~~−.05~~	+.05
	.05		.05

(d) A buffer has a pH of 3.17 and has the following concentrations.

1.0 *M* HF and 1.0 *M* NaF

32. A solution is prepared combining 500 mL of the buffer described above with 500 mL of distilled water to create a solution with a volume of 1000 mL. Do you predict that the pH of the final solution should be less than, equal to, or greater than 3.17? Justify your answer.

still have same C J to each other

33. Titration Practice

A 25.00mL sample of HNO_2 solution is titrated with 20.50mL of 0.250M NaOH solution to reach the equivalence point.

Write the titration reaction

$HNO_2 + NaOH \longrightarrow NaNO_2 + H_2O$

Write the reactions for Hydrolysis

$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$

Calculate the concentration of the original sample

$.250M\ NaOH = \frac{x\ mol}{.0205L} = .005125\ mol\ HNO_2$

$[HNO_2] = \frac{.005125\ mol}{.025L} = 0.205M$

Calculate the pH of the initial sample before any standard is added

HNO_2	$\rightleftharpoons$	NO_2^-	+	H^+
.205		0		0
$-x$		$+x$		$+x$
$.205-x$		x		x

$K_a = \frac{[H^+][NO_2^-]}{[HNO_2]} = \frac{x^2}{.205} = 4.6\times10^{-4}$

$x = 9.71\times10^{-3}M = [H_3O^+]$

$pH = 2.01$

Calculate the pH of the solution at the equivalence point

moles acid = moles base

$HNO_2 + NaOH \rightarrow NaNO_2 + H_2O$

$.005125 \quad .0072 \quad 0$

$\frac{.005125\ mol}{.025 + .025} = 0.113M$

$NO_2^- + H_2O \rightleftharpoons HNO_2 + OH^-$ — so base used NO_2^- K_b

.113		0	0
$-x$		$+x$	$+x$
$.113-x$		x	x

$1\times10^{-14} = 4.6\times10^{-4}(K_a)$

$K_b = 2.17\times10^{-11}$

$\frac{x^2}{.113} = 2.17\times10^{-11}$ $x = 1.57\times10^{-6}M = [OH^-]$

$pOH =$ $pH = 8.20$

Calculate the pH of the solution if 35.0mL of standard was added to the sample

$.250M = \frac{x}{.035L} = .00875\ mol\ NaOH$

$.005125\ mol\ HNO_2$

$HNO_2 + NaOH$

$.005125 \quad .00875$

$-.005125$

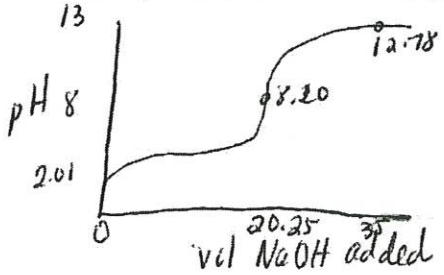
$\frac{.003625}{.060} = .0604M = [OH^-]$ xcess

$pOH = 1.21$

$pH = 12.78$

. Construct a titration curve for your sample. Be sure to include the following:

Title • Labeled axis • Correct scale • Smooth curve • Points plotted



34.

A 20.00mL sample of NH_3 solution is titrated with 25.0mL of 0.250M $HClO_4$ solution to reach the equivalence point

Write the titration reaction

$NH_3 + HClO_4 \rightarrow NH_4^+ + ClO_4^-$

Write the reactions for Hydrolysis

$NH_4^+ \rightarrow H^+ + NH_3$

Calculate the concentration of the original sample

$.250M = \frac{X}{.025L} = .00625mol$

$[NH_3] = \frac{.00625mol}{.0200} = .313M$

Calculate the pH of the initial sample before any standard is added

$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$

$K_b = \frac{1X10^{-14}}{5.6X10^{-10}} = 1.78X10^{-5}$

NH_3	H_2O	NH_4^+	OH^-
.313	X	0	0
$-X$		$+X$	$+X$
$.313-X$		X	X

$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{X^2}{.313} = 1.78X10^{-5}$ $X = .00236M = [OH^-]$ $pOH = 2.63$

$pH = 11.37$

Calculate the pH of the solution at the equivalence point

mole acid = mole base

Use K_a

$NH_3 + H^+ \rightarrow NH_4^+$

$.00625 \quad .00625$

$\frac{.00625mol}{.02 + .025} = .139M$

$NH_4^+ \rightarrow NH_3 + H^+$ K_a

NH_4^+	NH_3	H^+
.139	0	0
$-X$	$+X$	$+X$

$\frac{X^2}{.139} = \frac{5.6X10^{-10}}{K_a}$ $X = 8.819X10^{-6}M = [H_3O^+]$ $pH = 5.05$

Calculate the pH of the solution if 45.0mL of standard was added to the sample

$.250M\ HClO_4 = \frac{X}{.045} = \frac{.01125}{.045}$

$H^+ + NH_3 \rightarrow NH_4^+$

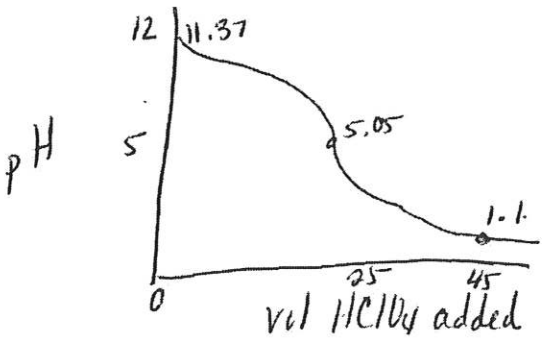
$.01125 \quad .00625$

$\frac{-.00625}{.005} = .07M$ $[H^+]$ excess

$pH = 1.1$

. Construct a titration curve for your sample. Be sure to include the following:

Title • Labeled axis • Correct scale • Smooth curve • Points plotted



KEY

Unit 9 Review

AP Chemistry: 9.1-9.3, 9.5, 7.14 Entropy and Gibbs Free Energy

1. Entropy Change Calculations

TABLE OF MOLAR ENTROPIES			
Substance	S° (J/mol-K)	Substance	S° (J/mol-K)
$H_2(g)$	130.6	$H_2O(l)$	69.9
$N_2(g)$	191.5	$H_2O(g)$	188.8
$O_2(g)$	205.0	$Na(s)$	51.3
$O_3(g)$	238.8	$Cl_2(g)$	223.0
$NH_3(g)$	192.5	$NaCl(s)$	72.1

For each of the following chemical reactions:

(a) Predict what should happen to the value of entropy change to the reaction. Should it be positive or negative? Justify your answer with the definition of entropy.

(b) Then, using the table, calculate the entropy change of reaction, ΔS°, for the chemical reaction

Chemical Reaction	*Entropy Change Prediction (+ or −)*	*Entropy Change Calculation*
$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$	*Negative, (−); less moles of gas are formed, and less freely moving particles.*	$\Delta S^\circ = [2 \times \Delta S(NH_3)] - [1 \times \Delta S(N_2) + 3 \times \Delta S(H_2)]$ $= [2 \times (192.5)] - [1 \times (191.5) + 3 \times (130.6)]$ $= -198.3$ J/mol-K
$2O_3(g) \longrightarrow 3O_2(g)$	+ more gas moles on products	$\Delta S = 3(205) - [2(238.8)] = 137.4$ J/mol·K
$H_2O(l) \longrightarrow H_2O(g)$	+ l→g more free movement	$\Delta S = 188.8 - 69.9 = 118.9$ J/mol·K
$2Na(s) + Cl_2(g) \longrightarrow 2NaCl(s)$	− g on reactants side only solid on products	$\Delta S = [2(72.1)] - [2(51.3) + 223] = -191.4$ J/K

Free Energy and Thermodynamic Favorability.

Substance	ΔG_f° (kJ/mol)
$H_2(g)$	0
$O_2(g)$	0
$H_2O(l)$	−237.2

2. Calculate the change in Gibb's Free Energy of the following reaction and identify whether it is thermodynamically favorable. $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$ $2(-237.2) - 0 = -474.4$ kJ/mol favorable

$-\Delta G$

3. Identify whether the reverse of the reaction in (2), shown below, is thermodynamically favorable.

No reverse would have $+\Delta G$ so not favorable

AP CHEM TIP: EVEN THOUGH A REACTION MAY BE SLOW, DOES NOT MEAN IT IS THERMODYNAMICALLY UNFAVORABLE. JUST BECAUSE A REACTION IS FAVORED, WE CANNOT SAY WHETHER THE REACTION OCCURS QUICKLY OR SLOWLY. IF THE ACTIVATION ENERGY IS RELATIVELY HIGH, THE REACTION WILL USUALLY OCCUR RATHER SLOWLY.

Recall: $\Delta G = \Delta H - T\Delta S$

$$CaCO_3(s) \longrightarrow CaO(s) + CO_2(g)$$

4. Using the thermodynamic data at left, calculate the change in Gibbs Free energy, ΔG° for the decomposition of calcium carbonate (above) and determine whether this reaction is thermodynamically favored to occur at 298 K.

Substance	ΔH_f° (kJ/mol)
$CaCO_3(s)$	- 1206.9
$CaO(s)$	- 634.9
$CO_2(g)$	- 393.5

Substance	S° (J/mol-K)
$CaCO_3(s)$	92.9
$CaO(s)$	38.1
$CO_2(g)$	213.8

$\Delta H = [-634.9 + 393.5] - [-1206.9] = +178.5\ kJ$

$\Delta S = [213.8 + 38.1] - [92.9] = 159.\ J/mol\cdot K$

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

$\Delta G = 178.5 - (298K)(.159\ kJ/mol\cdot K) = +131.12\ kJ$

Not $+\Delta G$ favorable

5. Is this decomposition of calcium carbonate thermodynamically favored to occur at 1000°C (1273 K)?

$178.5 - (1273K)(.159) = -23.91$ Yes

6. Determine the minimum temperature that would be required in order for this reaction to be thermodynamically favored. $0 = 178.5 - T(.159)$ $-178.5/-.159$ $T = 1122K$ or $849°C$

Keep in mind, when $\Delta G = 0$, then neither the forward or the reverse process is favored. Set $\Delta G = 0$ to find the "swing" temperature.

AP CHEMISTRY EXAM TIP:

You might see a question that asks you the following: **"What drives this reaction?"**

There will be three possible answers:

1. The reaction is driven by enthalpy only
   a. This only occurs when you have a **negative ΔH and negative ΔS**
2. The reaction is driven by entropy only
   a. This only occurs when you have a **positive ΔH and positive ΔS**
3. The reaction is driven both by enthalpy and entropy.
   a. This only occurs when you have a **negative ΔH and positive ΔS**

8. AP EXAM PRACTICE FRQ 9.1 - 9.3, 9.5, 7.14

$$NaHCO_3(s) + HC_2H_3O_2(aq) \longrightarrow NaC_2H_3O_2(aq) + H_2O(l) + CO_2(g)$$ ← more microstates so $+\Delta S$

A student designs an experiment to study the reaction between $NaHCO_3$ and $HC_2H_3O_2$. The reaction is represented by the equation above. The student places 2.24 g of $NaHCO_3$ in a flask and adds 60.0 mL of 0.875 M $HC_2H_3O_2$. The student observes the formation of bubbles and that the flask gets coolers as the reaction proceeds.

(a) In thermodynamic terms, a reaction can be driven by enthalpy, entropy, or both.

(i) Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$? Answer by drawing a circle around one of the choices below.

endothermic $+\Delta S$

Enthalpy only (Entropy only) Both enthalpy and entropy

(ii) Justify your selection in part (d)(i) in terms of ΔG.

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

$+ \quad + \quad$ so $-\Delta G$ $\quad$ $*T\Delta S > \Delta H$

a. This only occurs when you have a **negative ΔH° and positive ΔS°**

8. AP EXAM PRACTICE FRQ 9.1 - 9.3, 9.5, 7.14

$$NaHCO_3(s) + HC_2H_3O_2(aq) \longrightarrow NaC_2H_3O_2(aq) + H_2O(l) + CO_2(g)$$

A student designs an experiment to study the reaction between $NaHCO_3$ and $HC_2H_3O_2$. The reaction is represented by the equation above. The student places 2.24 g of $NaHCO_3$ in a flask and adds 60.0 mL of 0.875 M $HC_2H_3O_2$. The student observes the formation of bubbles and that the flask gets coolers as the reaction proceeds.

(a) In thermodynamic terms, a reaction can be driven by enthalpy, entropy, or both.

endothermic $+\Delta H$ more states so $+\Delta S$

(i) Considering that the flask gets cooler as the reaction proceeds, what drives the chemical reaction between $NaHCO_3(s)$ and $HC_2H_3O_2(aq)$? Answer by drawing a circle around one of the choices below.

Enthalpy only (Entropy only) Both enthalpy and entropy

(ii) Justify your selection in part (d)(i) in terms of ΔG°.

since $\Delta G = \Delta H - T\Delta S$ (+) (+) $-T\Delta S > \Delta H$ so $\Delta G = (-)$

Fulminic acid can convert to isocyanic acid according to the equation below.

$$HCNO(g) \rightleftarrows HNCO(g)$$

Fulminic acid *isocyanic acid*

Fulminic Acid	Isocyanic Acid
H—C≡N—Ö:	H—N̈=C=Ö:

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of ΔH° for the reaction of HCNO(g) to form HNCO(g). Bro kon formed

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N–O	201	C=N	615	H–C	413
C=O	745	C≡N	891	H–N	391

$[413+891+201] - [391+615+745]$

$1505 - 1751$

$-245 - 25$ J/mol

(c) A student claims that ΔS° for the reaction is close to zero. Explain why the student's claim is accurate.

both reactants + products are same state + same # moles

(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K. Justify your answer in terms of thermodynamic favorability and the equilibrium constant.

$-\Delta H + 0 = -\Delta G$ favorable

$K > 1$

Iso Cyanic acid

9. The student reads in a reference text that $NO(g)$ and $NO_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation.

$$NO(g) + NO_2(g) \rightleftarrows N_2O_3(g)$$

ΔH°_{298}	ΔS°_{298}	ΔG°_{298}
- 40.4 kJ/mol$_{rxn}$	- 138.5 J/(K·mol$_{rxn}$)	-0.87 kJ/mol$_{rxn}$

(a) The student begins with an equimolar mixture of $NO(g)$ and $NO_2(g)$ in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.

(i) Calculate the value of the equilibrium constant, K, for the reaction at 298 K.

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

$= 0.87$ K $K = \frac{-870}{8.314(298)}$

$K_p = \frac{P_{N_2O_3}}{P_{NO}\,P_{NO_2}}$

(ii) If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{N_2O_3}$ at equilibrium be equal to 1.0 atm? Justify your answer.

K is small so since $K < 1.0$ reactants will be present

(b) The student hypothesizes that increasing the temperature will increase the amount of $N_2O_3(g)$ in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

$-\Delta H$ so exo ↑ temp ← so it will decrease

9. Fulminic acid can convert to isocyanic acid according to the equation below.

$$HCNO(g) \rightleftarrows HNCO(g)$$

Fulminic acid *isocyanic acid*

Fulminic Acid	Isocyanic Acid
H—C≡N—Ö:	H—N̈=C=Ö:

(b) Using the Lewis electron-dot diagrams of fulminic acid and isocyanic acid shown in the boxes above and the table of average bond enthalpies below, determine the value of ΔH^o for the reaction of HCNO(*g*) to form HNCO(*g*). Broken – Formed

Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)	Bond	Enthalpy (kJ/mol)
N–O	201	C=N	615	H–C	413
C=O	745	C≡N	891	H–N	391

$[413+891+201]-[391+615+745]$
$1505 - 1751$
-245 kJ/mol

(c) A student claims that ΔS^o for the reaction is close to zero. Explain why the student's claim is accurate.
Both reactants & products are in same phase & same # moles

(d) Which species, fulminic acid (HCNO) or isocyanic acid (HNCO), is present in higher concentration at equilibrium at 298 K. Justify your answer in terms of thermodynamic favorability and the equilibrium constant. $\Delta G = \Delta H - T\Delta S$
$-\Delta H - 0 = -\Delta G$ favorable
so $K > 1$

10. The student reads in a reference text that NO(*g*) and $NO_2(g)$ will react as represented by the equation below. Thermodynamic data for the reaction are given in the table below the equation

$$NO(g) + NO_2(g) \rightleftarrows N_2O_3(g)$$

ΔH^o_{298}	ΔS^o_{298}	ΔG^o_{298}
– 40.4 kJ/mol$_{rxn}$	– 138.5 J/(K·mol$_{rxn}$)	+ 0.87 kJ/mol$_{rxn}$

(a) The student begins with an equimolar mixture of NO(*g*) and $NO_2(g)$ in a rigid reaction vessel and the mixture reaches equilibrium at 298 K.

(i) Calculate the value of the equilibrium constant, *K*, for the reaction at 298 K. $\Delta G = RT \ln K$ $K = e^{\frac{-\Delta G}{RT}}$
$K = e^{\frac{-870}{8.314(298)}} = .70$

(ii) If both P_{NO} and P_{NO_2} in the vessel are initially 1.0 atm, will $P_{N_2O_3}$ at equilibrium be equal to 1.0 atm? Justify your answer. $K_p = \frac{P_{N_2O_3}}{P_{NO}P_{NO_2}}$ K is small so since $K<1$ reactants will be present

(b) The student hypothesizes that increasing the temperature will increase the amount of $N_2O_3(g)$ in the equilibrium mixture. Indicate whether you agree or disagree with the hypothesis. Justify your answer.

11. $H_2NCONH_2(s) \rightleftarrows H_2NCONH_2(aq)$ $-\Delta H$ so exo ↑ temp ← so it will decrease

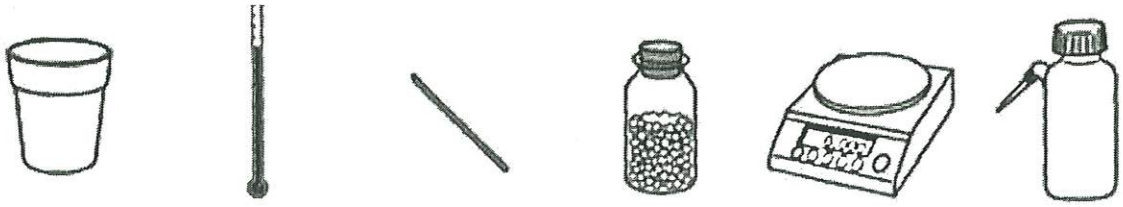
The dissolution of urea is represented by the equation above. A student determines that 5.39 grams of H_2NCONH_2 (molar mass 60.06 g/mol) can dissolve in water to make 5.00 mL of a saturated solution at 20°C.

(a) Calculate the concentrations of urea, in mol/L, in the saturated solution at 20°C.

$5.39\text{g}\ H_2NCONH_2 \left/ \frac{1\text{mol}}{60.06\text{g}} \right. = \frac{.0897\text{mol}}{.005\text{L}} = 17.9\ M$

(b) The student also determines that the concentration of urea in a saturated solution at 25°C is 19.8 *M*. Based on this information, is the dissolution of urea endothermic or exothermic? Justify your answer in terms of Le Chatelier's principle.

T↑ ↑ [ ] so more dissolves so → so endothermic



Polystyrene Cup | Thermometer | Stirring Rod | Bottle of Urea | Balance | Distilled Water

(c) The equipment shown above is provided so that the students can determine the value of the molar heat of solution for urea. Knowing that the specific heat of the solution is 4.18 J/(g·°C), list the specific measurements that are required to be made during the experiment. mass urea; initial + final temp; mass of water

	S° (J/mol-K)
$H_2NCONH_2(s)$	104.6
$H_2NCONH_2(aq)$	

(d) The entropy change for the dissolution of urea, ΔS°_{soln}, is 70.1 J/(mol·K) at 25°C. Using the information in the table above, calculate the absolute molar entropy, S°, of aqueous urea. $70.1 = P - 104.6 = 174.7$ J/mol K

(e) Using particle-level reasoning, explain why ΔS°_{soln} is positive for the dissolution of urea in water.

Solid → aqueous so more free movement + ΔS
more microstates or arrangements

(f) The student claims that ΔS° for the process contributes to the thermodynamic favorability of the dissolution of urea at 25°C. Use the thermodynamic information above to support the student's claim.

+ΔH so yes +ΔS TΔS and drives −ΔG value