



2014 U.S. NATIONAL CHEMISTRY OLYMPIAD NATIONAL EXAM - PART II



Prepared by the American Chemical Society Olympiad Examinations Task Force

OLYMPIAD EXAMINATIONS TASK FORCE

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DIRECTIONS TO THE EXAMINER - PART II

Part II of this test requires that student answers be written in a response booklet with blank pages. Only this "Blue Book" is graded for a score on **Part II**. Testing materials, scratch paper, and the "Blue Book" should be made available to the student only during the examination period. All testing materials including scratch paper should be turned in and kept secure until **April 28, 2014**, after which tests can be returned to students and their teachers for further study.

Allow time for the student to read the directions, ask questions, and fill in the required information on the "Blue Book". When the student has completed **Part II**, or after one hour and forty-five minutes have elapsed, the student must turn in the "Blue Book", **Part II** of the testing materials, and all scratch paper. Be sure that the student has supplied all of the information requested on the front of the "Blue Book," and that the same identification number used for **Part I** has been used again for **Part II**.

There are three parts to the National Olympiad Examination. You have the option of administering the three parts in any order, and you are free to schedule rest breaks between parts.

Part I	60 questions	single-answer multiple-choice	1 hour, 30 minutes
Part II	8 questions	problem-solving, explanations	1 hour, 45 minutes
Part III	2 lab questions	laboratory practical	1 hour, 30 minutes

A periodic table and other useful information are provided on page 4 for student reference.

Students should be permitted to use non-programmable calculators.

DIRECTIONS TO THE EXAMINEE

DO NOT TURN THE PAGE UNTIL DIRECTED TO DO SO. **Part II** requires complete responses to questions involving problem-solving and explanations. **One hour and forty-five minutes** are allowed to complete this part. Be sure to print your name, the name of your school, and your identification number in the spaces provided on the "Blue Book" cover. (Be sure to use the same identification number that was coded onto your Scantron sheet for **Part I**.) Answer all of the questions in order, and use both sides of the paper. Use separate sheets for scratch paper and do **not** attach your scratch paper to this examination. When you complete **Part II** (or at the end of one hour and forty-five minutes) you must turn in all testing materials, scratch paper, and your "Blue Book". **Do not forget to turn in your U.S. citizenship/ Green Card Holder statement before leaving the testing site today.**

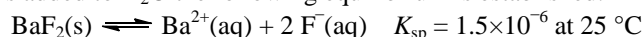
1. [13] When a mixture of a metal carbonate, MCO_3 , and its oxide, MO , is heated it releases carbon dioxide gas and is converted completely to the metallic oxide, MO .
- If a 0.6500 g sample of MCO_3 and MO forms 0.1575 L of carbon dioxide gas at 25.0 °C and a barometric pressure of 700.0 mm Hg, determine the number of moles of CO_2 formed.
 - When the 0.3891 g of MO resulting from the process in 1.a. is titrated with 0.500 M HCl , 38.60 mL are required. Determine the number of moles of MO in 0.3891 g.
 - Determine the atomic mass of the metal M and give its symbol.
 - Determine the mole percentages of MCO_3 and MO in the original sample.
 - The gas formed in 1.a. can be identified as CO_2 by means of infrared spectroscopy.
 - Sketch or describe the normal vibrations for the CO_2 molecule.
 - Identify the vibrations that are infrared active and outline your reasoning.

2. [14] Nitrogen forms many oxides, some of which are significant in the formation of photochemical smog. The ΔH_f° and ΔG_f° values for several of these nitrogen oxides are given in the table below.

	ΔH_f° , $\text{kJ}\cdot\text{mol}^{-1}$	ΔG_f° , $\text{kJ}\cdot\text{mol}^{-1}$
$\text{NO}_2(\text{g})$	33.85	51.84
$\text{N}_2\text{O}_4(\text{g})$	9.66	98.29
$\text{NO}(\text{g})$	90.37	86.71

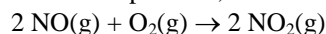
- Calculate the enthalpy and free energy changes at 25.0 °C for the
 - formation of $\text{NO}_2(\text{g})$ from $\text{NO}(\text{g})$ and $\text{O}_2(\text{g})$.
 - dimerization of $\text{NO}_2(\text{g})$ to form $\text{N}_2\text{O}_4(\text{g})$.
- Calculate the equilibrium constant for the dimerization of $\text{NO}_2(\text{g})$ at 25.0 °C.
- For an atmospheric concentration of NO_2 equal to 30. ppb (1.2×10^{-9} M) at 298 K, calculate the equilibrium concentration of N_2O_4 .
- If the atmospheric temperature increases to 43.0 °C and equilibrium is established, does the new concentration of nitrogen dioxide formed from conversion of N_2O_4 exceed the EPA limit of 53 ppb (2.2×10^{-9} M)? Explain.
- The positive ΔG_f° for NO_2 indicates that its decomposition to form the elements N_2 and O_2 is spontaneous. Suggest a reason that this process does not occur to a significant extent in the atmosphere once NO_2 has been formed.

3. [14] When solid BaF_2 is added to H_2O the following equilibrium is established.



- Calculate the molar solubility of barium fluoride at 25 °C.
 - Explain how adding each of the following substances affects the solubility of BaF_2 in water.
 - 0.10 M $\text{Ba}(\text{NO}_3)_2$
 - 0.10 M HNO_3
 - In an experiment to determine the K_{sp} of PbF_2 a student starts with 0.10 M $\text{Pb}(\text{NO}_3)_2$ and 0.10 M KF and uses the method of serial dilutions to find the lowest $[\text{Pb}^{2+}]$ and $[\text{F}^{-}]$ that form a precipitate when mixed. If the student uses the concentration of the ions in the combined solution to determine K_{sp} , will the value of K_{sp} calculated be too large, too small or just right? Explain.
 K_{sp} for $\text{PbF}_2 = 4.0 \times 10^{-8}$
 - In a solution of 0.010 M barium nitrate and 0.010 M lead(II) nitrate, which will precipitate first, BaF_2 or PbF_2 , as $\text{NaF}(\text{s})$ is added? Assume volume changes are negligible. Explain (support your answer with calculations).
 - When the more soluble fluoride begins to precipitate, what is the concentration of the cation for the less soluble fluoride that remains in solution?
4. [12] Amines are organic bases. Methylamine (CH_3NH_2) is the simplest amine.
- Write Lewis structures for methylamine and its conjugate acid, the methylammonium ion.
 - Describe the local geometry and hybridization of nitrogen in methylamine and the methylammonium ion.
 - Methylamine is a much stronger base than aniline ($\text{C}_6\text{H}_5\text{NH}_2$). Account for this observation on the basis of structure and bonding.
 - There are four isomeric amines with the formula $\text{C}_3\text{H}_9\text{N}$. Write condensed structural formulas for each and identify each structure as a primary, secondary, or tertiary amine.

5. [13] Consider the gas-phase reaction between nitric oxide and oxygen showing the initial concentrations of the reactants at a certain temperature, T:



Experiment	[NO], M	[O ₂], M	Initial Rate of NO ₂ formation, M•s ⁻¹
1	0.020	0.020	0.057
2	0.040	0.040	0.455
3	0.040	0.020	0.228

- a. Determine the order with respect to NO.
b. Determine the order with respect to O₂.
c. Calculate the rate constant and give its units at this temperature.
d. Calculate the initial rate of disappearance of O₂(g) in units of M•s⁻¹ for experiment 3.
e. If this reaction follows a two-step mechanism with the first step being $2 \text{NO} \rightleftharpoons \text{N}_2\text{O}_2$
i. Write an equation for the second step of the mechanism.
ii. Identify the rate determining step of this mechanism and outline your reasoning.
6. [10] Write net equations for each of the reactions below. Use ionic or molecular formulas as appropriate and omit formulas for any ions or molecules that do not take part in a reaction. Write structural formulas for all organic substances. You need not balance the equations or specify physical states.
- a. Aqueous silver acetate is mixed with aqueous sodium chromate.
b. Excess aqueous sodium oxalate is added to an aqueous solution of iron(III) nitrate.
c. Carbon dioxide is bubbled into an aqueous solution of calcium nitrate.
d. A solution of bromine in CHCl₃ is mixed with a solution of 1-butene in CHCl₃.
e. Uranium-235 is bombarded with a neutron to form one nucleus containing 54 protons and 83 neutrons plus a second nucleus and two neutrons.
7. [12] This question concerns the chemistry of the Group 13 elements (B - Tl). Base your answers on principles of atomic structure and bonding.
- a. The first ionization energies (IE) of most main group elements decrease steadily upon descending the family whereas the first IE of B-Tl are [B 801, Al 578, Ga 579, In 558, Tl 589] kJ•mol⁻¹.
i. Explain briefly why the IEs for most families decrease steadily upon descending a family.
ii. Suggest a reason that the IE for Ga is essentially the same as that for Al and the IE for Tl is greater than that for In.
b. The members of this family exhibit oxidation states of +1 and/or +3.
i. Account for the fact that the stable oxidation states are +1 and +3 and a +2 oxidation state is not observed.
ii. Account for the fact that B and Al show the +3 oxidation state exclusively while the +3 state for Tl is a strong oxidizing agent.
c. BCl₃ and AlCl₃ are strong Lewis acids.
i. Write an equation to illustrate BCl₃ acting as a Lewis acid with an appropriate Lewis base. Explain what occurs in a Lewis acid-base reaction.
ii. Account for the fact that the Lewis acidity of the other tri-chlorides decreases down the family.
8. [12] Explain each of the following observations using acid-base principles.
- a. The acids HCl and HBr appear equally strong in H₂O but HBr is a stronger acid in 100% (glacial) acetic acid.
b. The acidity of anhydrous H₂SO₄ is much less than the acidity of fuming H₂SO₄ (a saturated solution of SO₃ in H₂SO₄).
c. The first and second ionization constants for sulfurous acid, H₂SO₃(aq), differ by a factor of $\sim 2 \times 10^5$ while the first and second ionization constants of hydrosulfuric acid, H₂S(aq), differ by a much greater factor ($\sim 1 \times 10^{12}$).

ABBREVIATIONS AND SYMBOLS					
amount of substance	<i>n</i>	Faraday constant	<i>F</i>	molar mass	<i>M</i>
ampere	A	free energy	<i>G</i>	mole	mol
atmosphere	atm	frequency	ν	Planck's constant	<i>h</i>
atomic mass unit	u	gas constant	<i>R</i>	pressure	<i>P</i>
Avogadro constant	N_A	gram	g	rate constant	<i>k</i>
Celsius temperature	°C	hour	h	reaction quotient	<i>Q</i>
Centi-prefix	c	joule	J	second	s
coulomb	C	kelvin	K	speed of light	<i>c</i>
density	d	kilo-prefix	k	temperature, K	<i>T</i>
electromotive force	<i>E</i>	liter	L	time	<i>t</i>
energy of activation	E_a	measure of pressure mm Hg	mm Hg	vapor pressure	VP
enthalpy	<i>H</i>	milli-prefix	m	volt	V
entropy	<i>S</i>	molal	<i>m</i>	volume	<i>V</i>
equilibrium constant	<i>K</i>	molar	M		

CONSTANTS
$R = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$R = 0.0821 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
$1 F = 96,500 \text{ C}\cdot\text{mol}^{-1}$
$1 F = 96,500 \text{ J}\cdot\text{V}^{-1}\cdot\text{mol}^{-1}$
$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
$h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$
$c = 2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}$
$0^\circ\text{C} = 273.15 \text{ K}$
$1 \text{ atm} = 760 \text{ mm Hg}$

EQUATIONS

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

$$\ln K = \left(\frac{-\Delta H}{R} \right) \left(\frac{1}{T} \right) + \text{constant}$$

$$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

PERIODIC TABLE OF THE ELEMENTS

1																18	
1A											3A	4A	5A	6A	7A	8A	
1 H 1.008											13 B 10.81	14 C 12.01	15 N 14.01	16 O 16.00	17 F 19.00	2 He 4.003	
3 Li 6.941	4 Be 9.012											5 Al 26.98	6 Si 28.09	7 P 30.97	8 S 32.07	9 Cl 35.45	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3 B	4 C	5 N	6 O	7 F	8 Ne	9 Na	10 Mg	11 Al	12 Si	13 P	14 S	15 Cl	16 Ar		
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.88	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.39	31 Ga 69.72	32 Ge 72.61	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	56 Ba 137.3	57 La 138.9	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra (226)	89 Ac (227)	104 Rf (261)	105 Db (262)	106 Sg (271)	107 Bh (270)	108 Hs (277)	109 Mt (276)	110 Ds (281)	111 Rg (280)	112 Cn (285)	113 Uut (284)	114 Ff (289)	115 Uup (288)	116 Lv (293)	117 Uus (294)	118 Uuo (294)

58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm (145)	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.0	71 Lu 175.0
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np (237)	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (262)



1. a. $n = PV/RT = (700.0 \text{ mm Hg}/760 \text{ mm Hg/atm})(0.1575 \text{ L}) / [(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K})] = 0.00593 \text{ mol CO}_2$

Alternate approach $0.6500 \text{ g} - 0.3891 \text{ g} = 0.2609 \text{ g CO}_2$

$0.2609 \text{ g CO}_2 / 44.0 \text{ g/mole} = 0.00593 \text{ mole CO}_2$

b. $(0.500 \text{ mol/L})(0.03860 \text{ L}) = 0.01930 \text{ mol HCl}$
 $(0.01930 \text{ mol HCl})(1 \text{ mol MO} / 2 \text{ mol HCl}) = 0.00965 \text{ mol MO}$

c. $(0.3891 \text{ g MO}) / 0.00965 \text{ mol MO} = 40.32 \text{ g/mol MO}$
 $40.32 \text{ g/mol MO} - 16.0 \text{ g/mol O} = 24.32 \text{ g/mol M} \quad \text{M} = \text{Mg}^{2+}$

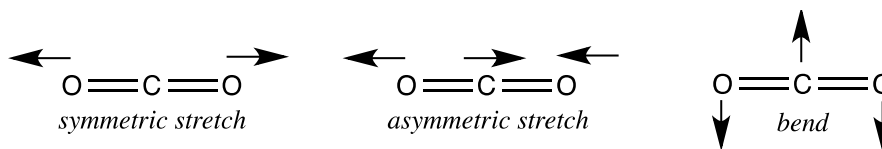
- d. Parts 1a-1c give three constraints on the number of moles of MgO and MgCO₃ present. From 1a, the total mass of the sample was 0.6500 g, so $(40.32 \text{ g/mol}) \times (n[\text{MgO}]) + (84.32 \text{ g/mol}) \times (n[\text{MgCO}_3]) = 0.6500 \text{ g}$. From 1b, the total number of moles of magnesium = $0.00965 \text{ mol} = n(\text{MgO}) + n(\text{MgCO}_3)$. From 1c, 0.00593 mol CO_2 implies $n(\text{MgCO}_3) = 0.005928 \text{ mol}$. Thus $n(\text{MgO}) = 0.00965 \text{ mol} - 0.005928 \text{ mol} = 0.00372 \text{ mol}$. Since one has three linear equations in two unknowns, one may use any two of the constraints to solve:

$$n(\text{MgO}) = 0.00372 \text{ mol}, n(\text{MgCO}_3) = 0.00593 \text{ mol}$$

$$\text{Mol \% MgO} = 0.00372 \text{ mol MgO} / 0.00965 \text{ moles total} = 0.385 \times 100\% = 38.5 \text{ mol\% MgO}$$

$$\text{Mol \% MgCO}_3 = 0.00593 \text{ mol MgCO}_3 / 0.00965 \text{ moles total} = 0.615 \times 100\% = 61.5 \text{ mol\% MgCO}_3$$

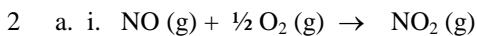
e. i.



- ii. The asymmetric stretch and bend are IR active because of change in dipole moment; the symmetric stretch is IR-inactive because it does not produce a change in dipole moment.

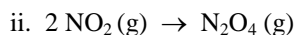


2014 U.S NATIONAL
CHEMISTRY OLYMPIAD
NATIONAL EXAM – PART II KEY



$$\Delta H^\circ_{\text{rxn}} = 33.85 \text{ kJ/mol} - 90.37 \text{ kJ/mol} = -56.52 \text{ kJ/mol}$$

$$\Delta G^\circ_{\text{rxn}} = 51.84 \text{ kJ/mol} - 86.71 \text{ kJ/mol} = -34.87 \text{ kJ/mol}$$



$$\Delta H^\circ_{\text{rxn}} = 9.66 \text{ kJ/mol} - 2(33.85 \text{ kJ/mol}) = -58.04 \text{ kJ/mol}$$

$$\Delta G^\circ_{\text{rxn}} = 98.29 \text{ kJ/mol} - 2(51.84 \text{ kJ/mol}) = -5.39 \text{ kJ/mol}$$

b. $\Delta G^\circ = -RT \ln K_{\text{eq}}$ Since the standard state for gases is 1 atm pressure, $K_{\text{eq}} = K_p$

$$-5390 \text{ J/mol} = -(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K}) \ln K_p$$

$$2.176 = \ln K_p$$

$$K_p = 8.81$$

c. $K_p = p(\text{N}_2\text{O}_4) / p(\text{NO}_2)^2 = 8.81$. If there is 30 ppb NO_2 , $p(\text{NO}_2) = (30 \times 10^{-9}) \times (1 \text{ atm}) = 3.0 \times 10^{-8} \text{ atm}$

$$p(\text{N}_2\text{O}_4) = 8.81 \times (3.0 \times 10^{-8})^2 = 7.9 \times 10^{-15} \text{ atm} = 7.9 \times 10^{-6} \text{ ppb}$$

$$[\text{N}_2\text{O}_4] = n/V = P/(RT) = 7.9 \times 10^{-15} \text{ atm}/(0.0821 \text{ L atm mol}^{-1} \text{ K}^{-1})(298 \text{ K}) = 3.2 \times 10^{-16} \text{ mol/L}$$

d. No. There is so little N_2O_4 (about 10 parts per billion of the total NO_2 !) that even if it all dissociates, it will have a negligible effect on the $[\text{NO}_2]$, which will remain 30 ppb (all the gases in the atmosphere change volume with temperature to approximately the same extent).

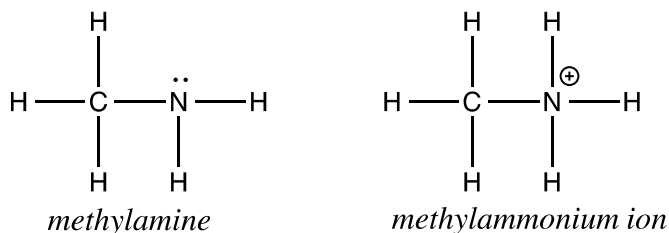
e. While the decomposition may be thermodynamically favorable, the reaction may be kinetically limited. That is, the reaction could lack a sufficient pathway (mechanism) to allow it to proceed.



- 3 a. If S = molar solubility of BaF_2 (s), then $[\text{Ba}^{2+}] = S$, $[\text{F}^-] = 2S$
 $K_{\text{sp}} = [\text{Ba}^{2+}][\text{F}^-]^2 = (S)(2S)^2 = 4S^3 = 1.5 \times 10^{-6}$
 $S = 0.00721 \text{ mol/L}$
- b. i. Adding Ba^{2+} ion will decrease the molar solubility of BaF_2 due to the common ion effect.
 ii. Adding H^+ will increase the molar solubility of BaF_2 as the F^- ion will react with H^+ to form HF , thereby causing more BaF_2 to dissolve by Le Chatelier's Principle.
- c. The calculated K_{sp} will be too large because the student is relying on seeing the formation of a precipitate at the moment that Q exceeds K_{sp} . The student will miss the exact moment that happens, so the calculated value of K_{sp} will be too large.
 Other possible issues: Protolysis will decrease the concentration of fluoride, so more fluoride will need to be added to cause precipitation; therefore measured K_{sp} will be too large. Likewise, some complex ions such as PbF^+ or PbF_2 (aq) may form, again leading to an experimental value that is too large.
- d. i. As both BaF_2 and PbF_2 are 1:2 compounds, and the concentrations of the metal ions are both 0.010 M, you can tell that PbF_2 will precipitate first, because it has the lower K_{sp} . For calculations to support this:
 For PbF_2 , $4.0 \times 10^{-8} = (0.01)[\text{F}^-]^2$ $[\text{F}^-]^2 = 4.0 \times 10^{-6}$ $[\text{F}^-] = 2.0 \times 10^{-3} \text{ M}$
 For BaF_2 , $1.5 \times 10^{-6} = (0.01)[\text{F}^-]^2$ $[\text{F}^-]^2 = 1.5 \times 10^{-4}$ $[\text{F}^-] = 1.2 \times 10^{-2} \text{ M}$
 The PbF_2 will precipitate first because a lower value for the concentration of fluoride is needed.
- ii. From part (i) we know that the BaF_2 precipitates second, when the $[\text{F}^-]$ reaches $1.2 \times 10^{-2} \text{ M}$
 Since PbF_2 (s) is present, then $[\text{Pb}^{2+}][\text{F}^-]^2 = K_{\text{sp}} = 4.0 \times 10^{-8}$
 $[\text{Pb}^{2+}](1.2 \times 10^{-2})^2 = 4.0 \times 10^{-8}$
 $[\text{Pb}^{2+}] = 2.8 \times 10^{-4} \text{ M}$



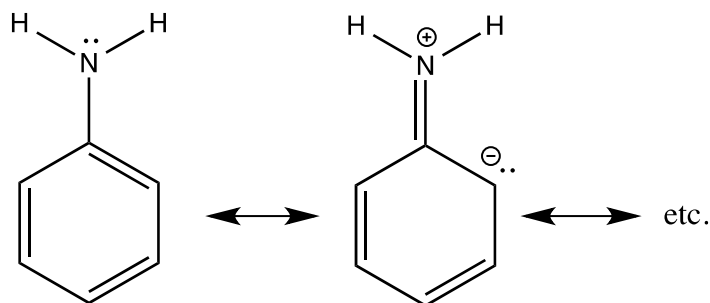
4 a.



b. In methylamine: N is trigonal pyramidal with sp^3 hybridization

In methylammonium ion: N is tetrahedral with sp^3 hybridization

c. In aniline, the lone pair is less accessible for donation, due to resonance between the lone pair on N and the benzene ring (see below). This resonance interaction is lost on protonation, which destabilizes the conjugate acid form and thus makes aniline less basic.



Less important considerations include: (1) A phenyl group is less electron donating than methyl since the sp^2 -hybridized carbon is more electronegative than the sp^3 carbon in methylamine. (2) The slightly larger size of phenyl vs. methyl might interfere with solvation of the charged conjugate acid, destabilizing the conjugate acid form of aniline relative to methylamine.

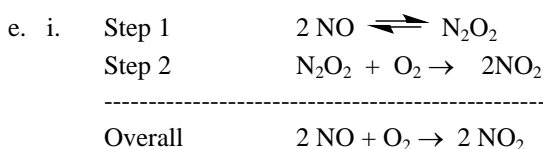
- d. $\text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2$: primary amine (propylamine)
 $\text{CH}_3\text{CH}(\text{CH}_3)\text{NH}_2$: primary amine (isopropylamine)
 $\text{CH}_3\text{NHCH}_2\text{CH}_3$: secondary amine (ethyl methyl amine)
 $(\text{CH}_3)_3\text{N}$: tertiary amine (trimethylamine)



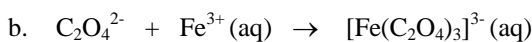
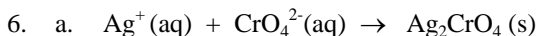
5. a. Comparing Expt. 1 and 3, doubling [NO] while keeping [O₂] constant shows a quadrupling of the rate. So reaction is second order in NO.
- b. Comparing Expt. 3 to Expt. 2, doubling [O₂] while keeping [NO] constant shows a doubling of the rate. So reaction is first order in O₂.

c. $\text{rate} = k[\text{NO}]^2[\text{O}_2]^1$
 $0.057 \text{ M/s} = k(0.020 \text{ M})^2 (0.020 \text{ M})^1$
 $k = 7.1 \times 10^3 \text{ M}^{-2} \text{ s}^{-1}$

- d. Rate of disappearance of O₂ is half of the rate of formation of NO, so 0.114 M s^{-1} .

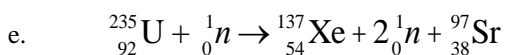
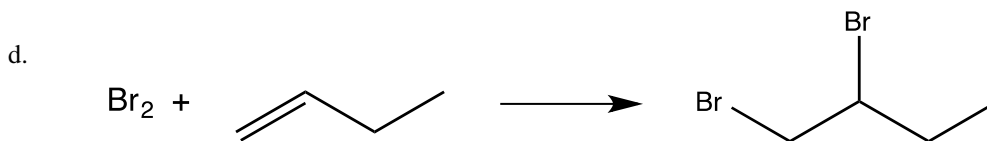


- ii. If step 1 is rate-limiting, then the predicted rate law is $k[\text{NO}]^2[\text{O}_2]^0$. If step 2 is rate-limiting, then the predicted rate law is $k[\text{NO}]^2[\text{O}_2]^1$. The latter is observed experimentally.



- c. Any of the following are reasonable:

- No reaction
- $\text{CO}_2 (\text{g}) + \text{H}_2\text{O} (\text{l}) \rightarrow \text{H}_2\text{CO}_3 (\text{aq})$
- $\text{CO}_2 (\text{g}) + \text{H}_2\text{O} (\text{l}) \rightarrow \text{H}^+ (\text{aq}) + \text{HCO}_3^- (\text{aq})$
- $\text{CaCO}_3 (\text{s})$ will NOT precipitate in the absence of base.





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- 7 a. i. When you descend families on the periodic table, the ionization of the electron occurs from higher n values that are (usually) further from the nucleus.
- ii. The $3d$ subshell fills just before Ga. There is no $2d$ subshell to fill prior to Al. The 10 added protons are not completely screened by the 10 d electrons, resulting in a higher effective nuclear charge and smaller radius than expected for Ga, hence a higher IE than expected. For Tl, the newly added subshell is the $4f$ subshell, and a similar effect is observed. [Relativistic effects also contribute to the higher IE of Tl.]
- b. i. The +1 ion corresponds to the loss of the np^1 electron, while +3 corresponds to the loss of the ns^2 and np^1 electrons. If 2 electrons were lost, a partially filled subshell would be present, which would interfere with bonding and would thus not be energetically favorable.
- ii. As one descends a column, the s electrons are more penetrating, held more tightly, and are therefore more difficult to lose. This is often called the “inert pair effect.”
- c. i. In a Lewis acid-base reaction, the Lewis base donates a pair of electrons to the Lewis acid, forming a new bond. Example (many others possible): $\text{BCl}_3 + \text{NH}_3 \rightarrow \text{BCl}_3 - \text{NH}_3$
- ii. The effectiveness of orbital overlap decreases down the family, so the bond between Lewis Acid and Lewis Base would weaken as the central atom of the acid gets larger.



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8. a. In water, both HCl and HBr are equally strong, because both are 100% ionized. Water is a “good enough” base to pull the hydrogen ion from those two molecules to about 100% efficiency (this is called "leveling"). In 100% (glacial) acetic acid the acetic acid is a much much weaker base than water. HCl only partially protonates acetic acid, while HBr more fully protonates it.



$\text{H}_2\text{S}_2\text{O}_7$ is a stronger acid than H_2SO_4 because there are more oxygens around the S holding the –OH bonds so the effective polarity of the –OH bond increases, making the molecule a stronger acid.

- c. In H_2SO_3 , the two hydrogens to be ionized are initially bonded to different atoms. Thus the negative charge left behind when the first H^+ is lost is (on average) farther away from the second H^+ and attracts it more weakly. In H_2S , both hydrogens to be lost are bonded to the same atom.