



International Chemistry Online Olympiad

Contest 1: Christmas 2013

December 21 to 28, 2013

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Instructions

Enclosed are 15 multiple-choice questions and 3 free-response questions. For the multiple-choice questions, respond with the letter of the correct choice. Explanations are not required. For the free-response questions, type up your full solutions. Submit your response via the provided form or to

iChOOContest@gmail.com

with your full name, member code, age and grade. For each multiple-choice question, a correct answer will earn you 3 points, an incorrect answer will be penalized by 1 point, and leaving it unanswered will give you 0 points. For each free-response question, depending on your steps and correctness of your work, you will get a score between 0 and 10 points, inclusive. Thus, the maximum possible score is 75. The top 3 will receive IChOO T-shirts, courtesy of Brilliant.org.

Although you have a week for this, you should be able to complete this entire set within 2 hours. Plus, it's holiday season so relax and have fun; happy holidays! Note that the next two pages contain useful information you may need on the contest. Further information should not be looked up.

Periodic Table of Elements

hydrogen 1 H 1.0079																		helium 2 He 4.0026			
lithium 3 Li 6.941		beryllium 4 Be 9.0122																			
sodium 11 Na 22.990		magnesium 12 Mg 24.305																			
potassium 19 K 39.098		calcium 20 Ca 40.078		scandium 21 Sc 44.956	titanium 22 Ti 47.867	vanadium 23 V 50.942	chromium 24 Cr 51.996	manganese 25 Mn 54.938	iron 26 Fe 55.845	cobalt 27 Co 58.933	nickel 28 Ni 58.693	copper 29 Cu 63.546	zinc 30 Zn 65.39	gallium 31 Ga 69.723	germanium 32 Ge 72.61	arsenic 33 As 74.922	selenium 34 Se 78.96	bromine 35 Br 79.904	krypton 36 Kr 83.80		
rubidium 37 Rb 85.468		strontium 38 Sr 87.62		ytrium 39 Y 88.906	zirconium 40 Zr 91.224	niobium 41 Nb 92.906	molybdenum 42 Mo 95.94	technetium 43 Tc [98]	ruthenium 44 Ru 101.07	rhodium 45 Rh 102.91	palladium 46 Pd 106.42	silver 47 Ag 107.87	cadmium 48 Cd 112.41	indium 49 In 114.82	tin 50 Sn 118.71	antimony 51 Sb 121.76	tellurium 52 Te 127.60	iodine 53 I 126.90	xenon 54 Xe 131.29		
cesium 55 Cs 132.91		barium 56 Ba 137.33		57-70 *		lutetium 71 Lu 174.97	hafnium 72 Hf 178.49	tantalum 73 Ta 180.95	tungsten 74 W 183.84	rhenium 75 Re 186.21	osmium 76 Os 190.23	iridium 77 Ir 192.22	platinum 78 Pt 195.08	gold 79 Au 196.97	mercury 80 Hg 200.59	thallium 81 Tl 204.38	lead 82 Pb 207.2	bismuth 83 Bi 208.98	polonium 84 Po [209]	astatine 85 At [210]	radon 86 Rn [222]
francium 87 Fr [223]		radium 88 Ra [226]		89-102 * *		lawrencium 103 Lr [260]	rutherfordium 104 Rf [261]	dubnium 105 Db [262]	seaborgium 106 Sg [266]	bohrium 107 Bh [264]	hassium 108 Hs [277]	meitnerium 109 Mt [268]	unnilennium 110 Uu [271]	ununium 111 Uu [272]	unbibium 112 Uu [273]	unreached 114 Uu [289]					

*Lanthanide series

lanthanum 57	cerium 58	praseodymium 59	neodymium 60	promethium 61	samarium 62	eucptium 63	gadolinum 64	terbium 65	dysprosium 66	holmium 67	erbium 68	thulium 69	yterbium 70
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
138.91	140.12	140.91	144.24	144.91	150.36	151.96	157.25	158.93	162.50	164.93	167.26	168.93	173.05
actinium 89	thorium 90	protactinium 91	uranium 92	neptunium 93	plutonium 94	americium 95	curium 96	berkelium 97	californium 98	astatine 99	fermium 100	mendelevium 101	nobelium 102
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
227.03	232.04	231.04	238.03	237.05	244.06	243.06	247.07	247.07	251.08	252.08	257.10	259.10	262.11

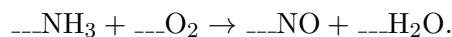
** Actinide series

Standard Reduction Potentials in Aqueous Solution at 25°C

Reduction Half-Reaction	E° (V)
$\text{F}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{F}^-(\text{aq})$	+2.87
$\text{H}_2\text{O}_2(\text{aq}) + 2 \text{H}_3\text{O}^+(\text{aq}) + 2 \text{e}^- \rightarrow 4 \text{H}_2\text{O}(\ell)$	+1.77
$\text{PbO}_2(\text{s}) + \text{SO}_4^{2-}(\text{aq}) + 4 \text{H}_3\text{O}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 6 \text{H}_2\text{O}(\ell)$	+1.685
$\text{MnO}_4^-(\text{aq}) + 8 \text{H}_3\text{O}^+(\text{aq}) + 5 \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 12 \text{H}_2\text{O}(\ell)$	+1.52
$\text{Au}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Au}(\text{s})$	+1.50
$\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq})$	+1.360
$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14 \text{H}_3\text{O}^+(\text{aq}) + 6 \text{e}^- \rightarrow 2 \text{Cr}^{3+}(\text{aq}) + 21 \text{H}_2\text{O}(\ell)$	+1.33
$\text{O}_2(\text{g}) + 4 \text{H}_3\text{O}^+(\text{aq}) + 4 \text{e}^- \rightarrow 6 \text{H}_2\text{O}(\ell)$	+1.229
$\text{Br}_2(\ell) + 2 \text{e}^- \rightarrow 2 \text{Br}^-(\text{aq})$	+1.08
$\text{NO}_3^-(\text{aq}) + 4 \text{H}_3\text{O}^+(\text{aq}) + 3 \text{e}^- \rightarrow \text{NO}(\text{g}) + 6 \text{H}_2\text{O}(\ell)$	+0.96
$\text{OCl}^-(\text{aq}) + \text{H}_2\text{O}(\ell) + 2 \text{e}^- \rightarrow \text{Cl}^-(\text{aq}) + 2 \text{OH}^-(\text{aq})$	+0.89
$\text{Hg}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Hg}(\ell)$	+0.855
$\text{Ag}^+(\text{aq}) + \text{e}^- \rightarrow \text{Ag}(\text{s})$	+0.80
$\text{Hg}_2^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{Hg}(\ell)$	+0.789
$\text{Fe}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{Fe}^{2+}(\text{aq})$	+0.771
$\text{I}_2(\text{s}) + 2 \text{e}^- \rightarrow 2 \text{I}^-(\text{aq})$	+0.535
$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\ell) + 4 \text{e}^- \rightarrow 4 \text{OH}^-(\text{aq})$	+0.40
$\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$	+0.337
$\text{Sn}^{4+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}^{2+}(\text{aq})$	+0.15
$2 \text{H}_3\text{O}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g}) + 2 \text{H}_2\text{O}(\ell)$	0.00
$\text{Sn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Sn}(\text{s})$	-0.14
$\text{Ni}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Ni}(\text{s})$	-0.25
$\text{V}^{3+}(\text{aq}) + \text{e}^- \rightarrow \text{V}^{2+}(\text{aq})$	-0.255
$\text{PbSO}_4(\text{s}) + 2 \text{e}^- \rightarrow \text{Pb}(\text{s}) + \text{SO}_4^{2-}(\text{aq})$	-0.356
$\text{Cd}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cd}(\text{s})$	-0.40
$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Fe}(\text{s})$	-0.44
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Zn}(\text{s})$	-0.763
$2 \text{H}_2\text{O}(\ell) + 2 \text{e}^- \rightarrow \text{H}_2(\text{g}) + 2 \text{OH}^-(\text{aq})$	-0.8277
$\text{Al}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Al}(\text{s})$	-1.66
$\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mg}(\text{s})$	-2.37
$\text{Na}^+(\text{aq}) + \text{e}^- \rightarrow \text{Na}(\text{s})$	-2.714
$\text{K}^+(\text{aq}) + \text{e}^- \rightarrow \text{K}(\text{s})$	-2.925
$\text{Li}^+(\text{aq}) + \text{e}^- \rightarrow \text{Li}(\text{s})$	-3.045

Multiple-Choice Questions.

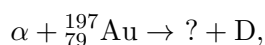
1. Nitric acid is an important inorganic acid. A major industrial method for producing nitric acid is through the multi-step Ostwald process. The first step of the process involves heating ammonia, in the following unbalanced chemical equation:



What is the sum of the coefficients when the equation is balanced with the smallest integer values?

- (A) 7 (B) 14 (C) 19 (D) 38
2. Which of the following statement(s) is/are true?
- I. Esterification of carboxylic acids produces the hydroxyl functional group
II. Esterification of alcohols produces the carbonyl functional group
III. Esterification to yield alcohols produces the carboxyl functional group
- (A) I only (B) I and II only (C) II and III only (D) I, II, and III
3. In an experiment I was able to produce liquid oxygen in a test tube. Using test tube clamps, I poured the oxygen between 2 poles of a magnet. Instead of seeping through, some of the liquid oxygen was caught in between the poles of the magnet. What property of O_2 best explains this phenomenon?
- (A) O_2 molecules are polar
(B) O_2 molecules are paramagnetic
(C) O_2 molecules bind strongly with magnets
(D) O_2 molecules are diamagnetic

4. Fill in the missing particle:



where D is a Deuterium nucleus.

- (A) ${}^{198}_{79}\text{Au}$ (B) ${}^{198}_{80}\text{Hg}$ (C) ${}^{199}_{80}\text{Hg}$ (D) ${}^{200}_{80}\text{Hg}$
5. Which reaction involves an increase in entropy?
- (A) $\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g)$
(B) $2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g)$
(C) $\text{C}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g)$
(D) $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$

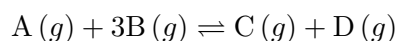
6. X-rays of wavelength 154 fm strike an aluminum crystal. The rays are reflected at an angle of 19.3 degrees. Calculate the minimal spacing between the planes of the lattice of aluminum atoms responsible for this angle of reflection.

(A) 108 fm (B) 233 fm (C) 324 fm (D) 466 fm

7. The molecular shape of PO_4^{-3} can best be described as

(A) bent (B) tetrahedral (C) trigonal bipyramidal (D) trigonal pyramidal

8. Consider the equilibrium equation



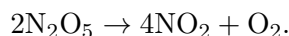
that is completely balanced and A, B, C, and D are gaseous compounds or elements. The reaction is exothermic, with $\Delta H = -201.3 \text{ kJ/mol}$. Consider the following changes on the reaction.

- I. Increasing the concentration of B
- II. Decreasing the concentration of D
- III. Decreasing the temperature of the surroundings

Which of the above changes will make the equilibrium state tend towards the same direction (forwards / backwards) as increasing the pressure on the system?

(A) I only (B) I and II only (C) I, II, and III (D) None

9. One way of producing NO_2 is by the decomposition of dinitrogen pentoxide. The equation for this reaction is



The decomposition of N_2O_5 is a first order reaction with rate constant $5.1 \times 10^{-4} \text{ s}^{-1}$ at 45 degrees celsius. If the initial concentration of N_2O_5 is 0.50 M, what is its concentration after 6.4 minutes?

(A) 0.032 (B) 0.187 (C) 0.338 (D) 0.442

10. Aniline reacts, in presence of Br_2/CCl_4 to produce 2,4,6-tribromoaniline, a white precipitate. Consider a specimen of aniline of volume 20 mL, which reacted with 50 mL of a Bromine solution to produce 3.3 mg of the white precipitate. If x is the concentration of the aniline solution in Molar, and y is the concentration of the Bromine solution in Molar, then
- (A) $x = 5 \times 10^{-6}$, $y = 6 \times 10^{-6}$
(B) $x = 10^{-5}$, $y = 6 \times 10^{-6}$
(C) $x = 5 \times 10^{-4}$, $y = 6 \times 10^{-4}$
(D) $x = 10^{-5}$, $y = 6 \times 10^{-4}$
11. The pK_w of water at 50°C is 13.26. What is the pH of a $1.00 \cdot 10^{-6}\text{ M Ba(OH)}_2$ solution at this temperature?
- (A) 7.26 (B) 7.56 (C) 8.00 (D) 8.30
12. How many different electronic states are possible for a given principal quantum number, n ?
- (A) n (B) $2n$ (C) n^2 (D) $2n^2$
13. Which of the following species exists in the most stereoisomeric forms?
- (A) $[\text{Pt}(\text{NH}_3)_4\text{ClBr}]^+$ (B) $\text{Pt}(\text{NH}_3)_3\text{Cl}_2\text{Br}$
(C) $[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]^+$ (D) $[\text{Pt}(\text{NH}_3)_2\text{ClBr}]^+$
14. Which of the following reactions produces *o*-nitro aniline as the major product in a good yield and in an efficient manner?
- (A) $\text{PhNH}_2 + \text{HNO}_3 + \text{H}_2\text{SO}_4 \xrightarrow{0-5^\circ\text{C}} ?$
(B) $\text{PhNH}_2 \xrightarrow{\text{Ac}_2\text{O}} ? \xrightarrow{\text{HNO}_3/\text{H}_2\text{SO}_4} ? \xrightarrow{\text{H}_2\text{O}} ?$
(C) $\text{PhNO}_2 + \text{HNO}_3 + \text{H}_2\text{SO}_4 \xrightarrow{0-5^\circ\text{C}} ? \xrightarrow{\text{Fe/HCl}} ?$
(D) $\text{PhNO}_2 + \text{HNO}_3 + \text{H}_2\text{SO}_4 \xrightarrow{0-5^\circ\text{C}} ? \xrightarrow{\text{Cu/HBr}} ?$
15. Which of the following organic transformations cannot happen in basic solution?
- (A) Alkene Hydration (B) Amide Hydrolysis
(C) Epoxide ring-opening (D) Aldol Condensation
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Free-response.

Problem 1 (Producing Hydrogen). About 75% of hydrogen is produced by the steam-reforming process. In this process, a mixture of methane and water is reacted at high temperatures to form carbon monoxide and hydrogen. This reaction is carried out in two stages. In the primary stage, a mixture of steam and methane at about 30 atm is heated over a nickel catalyst at 800° C to produce hydrogen and carbon monoxide. The secondary stage is carried out at approximately 1000° C to convert the remaining methane to hydrogen. The ΔH value in the primary reaction is 206 kJ, while the ΔH value in the secondary reaction is 35.7 kJ.

- (a) Write the balanced equation for the primary and secondary stage using the smallest whole coefficients (You do not need to indicate their physical states)
- (b) Under what conditions would favor the formation of products in both the primary and secondary stage? (Think in terms of temperature and pressure)
- (c) The equilibrium constant (K_c) for the primary stage is approximately 18 at 800° C. Calculate K_p for the reaction.
- (d) Given the partial pressures of methane and steam were both 20 atm at the start, use your answer in (c) to find what the pressure of CH_4 is at equilibrium.

Note: If your answer in part c is incorrect however your answer for part d using your wrong answer from part c is “correct,” then you may still receive full credit for part (d).

Problem 2 (Equilibrium Dissociation of CO_2). When iron (II) oxide, FeO , is heated at 1000 K, the equilibrium oxygen pressure over the compound is $4.10 \cdot 10^{-16}$ Pa.

- (a) Write the overall reaction that occurs. Calculate the equilibrium constant (K_p) and ΔG° for this reaction at 1000 K.

Now, an equilibrium mixture of CO_2 and CO gases over FeO at 1000 K and atmospheric pressure contains 60% CO by moles.

- (b) Write the overall reaction occurring. Calculate the equilibrium constant of this process (K_p).
- (c) What is K_d for the dissociation of CO_2 to oxygen and carbon monoxide under these conditions (1000 K, 1 atm)? Assume 1 mole of O_2 is produced.
- (d) Estimate the degree of dissociation of CO_2 to oxygen and carbon monoxide under these conditions.

- (e) What is the degree of dissociation of CO_2 when the pressure is increased to 10 atm?
- (f) Is it possible to calculate the dissociation constant at 600 K and 1 atm? If yes, calculate the value. If not, indicate what additional data is needed.
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Problem 3 (Solution of Benzoic Acid).

(a) A solution of 0.15 moles of benzoic acid (PhCOOH) is treated with 0.01 moles of NaOH in 500 mL of water. Write the net ionic equation that occurs.

(b) The pK_a of benzoic acid is 4.2. Determine the concentrations of each of the following species in solution once equilibrium is established in part (a):

$$(i)[\text{Na}^+], \quad (ii)[\text{PhCOOH}], \quad (iii)[\text{PhCOO}^-], \quad (iv)[\text{OH}^-].$$

(c) Calculate the pH after an additional 0.04 moles of NaOH are added. Assume volume change is negligible.

(d) You hope to buffer the solution at $pH = 9.0$. How much additional NaOH (in moles) needs to be added to achieve this pH ? Will it be an effective buffer? Explain.

(e) A different buffered solution is made by adding a small amount of NaOH to a mixture of acetic acid ($pK_a = 4.8$) and benzoic acid. The final pH measured by calomel electrode is 4.60. Determine the ratios of $[\text{PhCOOH}]$ to $[\text{PhCOO}^-]$ and $[\text{AcOH}]$ to $[\text{AcO}^-]$ in the solution.
