



ACS USNCO
U.S. National Chemistry Olympiad

2021 U.S. NATIONAL CHEMISTRY OLYMPIAD NATIONAL EXAM PART II

Prepared by the American Chemical Society Chemistry Olympiad Examinations Task Force

OLYMPIAD EXAMINATIONS TASK FORCE

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The 2021 National Examination was modified so it could be conducted digitally. The following describes this exam as given this year. Part III was removed from the examination, and time limits remained the same for Part I and Part II. This file was published for record keeping purposes after the examination was complete.

The periodic table and other useful information, as shown on page 2 of this document, were included for student reference on both Part I and Part II.

National Exam Nominee agreement forms, which required students to certify that they are either U.S. citizens or permanent residents, were collected prior to the administration of Part I.

For Part I and Part II, students were permitted to use only non-programmable calculators. The use of a programmable calculator, or accessing information outside of the standard reference document, was grounds for disqualification.

Part I of this test was administered through the ACS Learning Center and consisted of 60 multiple-choice questions. Answers were entered using this system and only submitted answers were considered (i.e. no scratch paper was accepted). This test was held for the majority of students on Saturday, April 17, 2021. The time limit was **one hour and thirty minutes**.

Part II was administered solely to the top 200 performing students on Part I. This was done using an online system that required students to complete the exam on their own paper, then upload one PDF file per question. The time limit for this part of the exam, which included 8 questions, remained at **one hour and forty-five minutes**.

Invitation to take Part II did NOT signify that a student earned the honors or high honors recognitions. As always, these consider performance on the full examination.

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

CONSTANTS
$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$
$R = 0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1}$
$F = 96,500 \text{ C mol}^{-1}$
$F = 96,500 \text{ J V}^{-1} \text{ mol}^{-1}$
$N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$
$h = 6.626 \times 10^{-34} \text{ J s}$
$c = 2.998 \times 10^8 \text{ m s}^{-1}$
$0 \text{ }^\circ\text{C} = 273.15 \text{ K}$
$1 \text{ atm} = 1.013 \text{ bar} = 760 \text{ mm Hg}$
Specific heat capacity of $\text{H}_2\text{O} = 4.184 \text{ J g}^{-1} \text{ K}^{-1}$

EQUATIONS		
$E = E^\circ - \frac{RT}{nF} \ln Q$	$\ln K = \left(\frac{-\Delta H^\circ}{R} \right) \left(\frac{1}{T} \right) + \text{constant}$	$\ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$

PERIODIC TABLE OF THE ELEMENTS

1	PERIODIC TABLE OF THE ELEMENTS																18										
1A															8A												
1 H 1.008	2 He 4.003																										
3 Li 6.941	4 Be 9.012	13 B 10.81	14 C 12.01	15 N 14.01	16 O 16.00	17 F 19.00	18 Ne 20.18																				
11 Na 22.99	12 Mg 24.31	3 B 10.81	4 C 12.01	5 N 14.01	6 O 16.00	7 F 19.00	8 Ne 20.18	9 Al 26.98	10 Si 28.09	11 P 30.97	12 S 32.07	13 Cl 35.45	14 Ar 39.95														
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 78.97	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 95.95	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 (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)	110 Ds (281)	111 Rg (272)	112 Cn (285)	113 Nh (286)	114 Fl (289)	115 Mc (289)	116 Lv (293)	117 Ts (294)	118 Og (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. [12%] A binary oxide X_mO_n is a white, slightly volatile solid that reacts with saturated aqueous $Ba(OH)_2$ to give a white precipitate.
- A 69.5 mg sample of this oxide is placed in an evacuated 1.00 L container, which is then heated slowly until the solid just vaporizes completely. At this point, the pressure in the container is 20.0 mm Hg and the temperature is 239.7 °C. What is the molar mass of the oxide in the gas phase?
 - A 1.00 g sample of the oxide is dissolved in aqueous acid and electrolytically reduced, with elemental X depositing on the cathode. Complete electrolysis requires 58 minutes with a current of 1.00 A. What is the value of n in the formula X_mO_n ?
 - What is the chemical formula of the oxide?
 - Write a balanced net ionic equation for the reaction of the oxide with a saturated aqueous solution of $Ba(OH)_2$.
 - The experiment described in part (a) is repeated with a 415.7 mg sample of the oxide, which requires heating to 280.0 °C to just vaporize the solid. What is the standard enthalpy of sublimation of the oxide?
2. [12%] A saturated aqueous solution of $Ca(OH)_2$ has pH = 12.40.
- What is the concentration of hydroxide ion in this solution?
 - What is the K_{sp} of $Ca(OH)_2$?
- A 100.0 mg sample of $Ca(OH)_2$ ($M = 74.09$) is suspended in 100.0 mL of water. The mixture is stirred vigorously and 3 M sulfuric acid is added dropwise to it while monitoring the pH of the solution.
- At the point that the pH reaches 7.00, there is solid calcium sulfate suspended in the solution. What is the concentration of $Ca^{2+}(aq)$ in the solution at this point? The K_{sp} of $CaSO_4$ is 2.4×10^{-5} .
 - Does the solution become homogeneous at any point during this titration? Justify your answer.
3. [13%] Vanadium can adopt four oxidation states in aqueous solution.

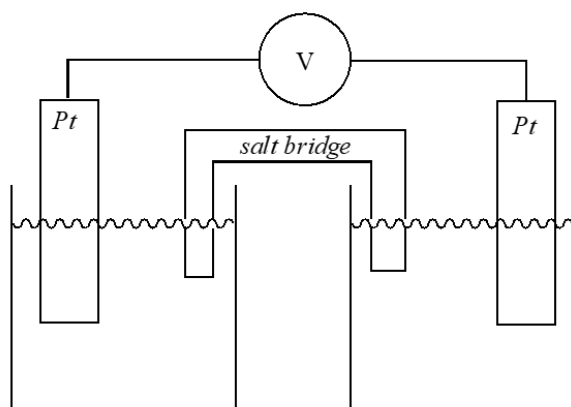
Half-reaction	E° at 298 K, V
$VO_2^+(aq) + 2 H^+(aq) + e^- \rightarrow VO^{2+}(aq) + H_2O(l)$	+1.00
$VO^{2+}(aq) + 2 H^+(aq) + e^- \rightarrow V^{3+}(aq) + H_2O(l)$	+0.34
$V^{3+}(aq) + e^- \rightarrow V^{2+}(aq)$	-0.26

- Calculate E° for the following half-cell at 298 K:

$$VO_2^+(aq) + 4 H^+(aq) + 3 e^- \rightarrow V^{2+}(aq) + 2 H_2O(l) \quad E^\circ = ???$$
- A vanadium battery can be constructed using the reduction of vanadium(V) by vanadium(II). Calculate ΔE° for this reaction at 298 K:

$$VO_2^+(aq) + V^{2+}(aq) + 2 H^+(aq) \rightarrow VO^{2+}(aq) + V^{3+}(aq) + H_2O(l)$$
- The value of ΔE° for the vanadium battery increases with increasing temperature by $1.76 \times 10^{-4} \text{ V K}^{-1}$. Calculate $\Delta H^\circ_{\text{rxn}}$ and $\Delta S^\circ_{\text{rxn}}$ for the vanadium battery.

A vanadium battery is set up as shown below [next page], using solutions that are buffered at pH = 1.00. It is then discharged with a constant current of 10.0 A until the cell potential reaches 1.14 V. The temperature is maintained at 298 K, and the volume of solution in each beaker is 100.0 mL.



Initial conditions: $[\text{VO}_2^+] = 0.50 \text{ M}$ $[\text{V}^{2+}] = 0.50 \text{ M}$
 $[\text{VO}^{2+}] = 0.10 \text{ M}$ $[\text{V}^{3+}] = 0.10 \text{ M}$
 $\text{pH} = 1.00$ $\text{pH} = 1.00$
 $\text{volume} = 100.0 \text{ mL}$ $\text{volume} = 100.0 \text{ mL}$

- What is the concentration of $\text{V}^{3+}(\text{aq})$ in the anodic cell when the cell voltage reaches 1.14 V?
- How much time is required to achieve this voltage?

4. [13%] The gas-phase equilibrium between nitryl chloride (NO_2Cl) and nitrosyl chloride (NOCl) was studied:



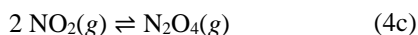
The equilibrium constant for reaction 4a was measured as $K_{4\text{a}} = 1.12 \times 10^4$ at 298 K and $K_{4\text{a}} = 4.68 \times 10^3$ at 340 K.

- Calculate $\Delta G^\circ_{4\text{a}}$ at both 298 K and 340 K.
- Calculate $\Delta H^\circ_{4\text{a}}$ and $\Delta S^\circ_{4\text{a}}$ (assuming that they are essentially independent of temperature).
- Which of the four gaseous compounds involved in this equilibrium has the lowest standard molar entropy S° at 298 K? Justify your choice.
- The normal boiling point of NOCl is -6°C . Consider reaction 4b that produces liquid NOCl rather than gaseous NOCl :



At 298 K, how will each of the thermodynamic quantities $\Delta H^\circ_{4\text{b}}$, $\Delta S^\circ_{4\text{b}}$, and $\Delta G^\circ_{4\text{b}}$ compare to the corresponding thermodynamic quantity for reaction 4a (i.e., will the quantity for 4b be greater than, less than, or equal to the quantity for 4a)? Justify your answers.

- In experimental practice, the study of equilibrium 4a is complicated by the fact that $\text{NO}_2(\text{g})$ is also in equilibrium with $\text{N}_2\text{O}_4(\text{g})$ according to reaction 4c under conditions where reaction 4a attains equilibrium.



Suppose that samples of NO_2Cl and NO are introduced into a reaction vessel and the mixture is allowed to attain equilibrium according to reactions 4a and 4c at 320 K. If the volume of the reaction vessel is doubled, will the number of moles of $\text{NOCl}(\text{g})$ increase, decrease, or stay the same after the system reattains equilibrium? Justify your answer.

- [12%] Write net equations for each of the reactions below. Use appropriate ionic and molecular formulas and omit formulas for all ions or molecules that do not take part in a reaction. Write structural formulas for all organic substances. You need not balance the equations.
 - Solid calcium oxide is added to distilled water.
 - Acidic aqueous solutions of potassium permanganate and iron(II) sulfate are mixed.

- c. Gaseous ammonia and boron trifluoride are mixed.
- d. Solid phosphorus(V) oxide is added to an excess of aqueous sodium carbonate.
- e. Potassium hydroxide is added to a dimethyl sulfoxide solution of 1-bromobutane.
- f. Fluorine-18 emits a positron.

6. [13%] Explain the following observations about complex ions of the transition metals.

- a. The $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ion is paramagnetic while the $\text{Sc}(\text{H}_2\text{O})_6^{3+}$ ion is diamagnetic.
- b. The CoF_6^{3-} ion is paramagnetic while the $\text{Co}(\text{CN})_6^{3-}$ ion is diamagnetic.
- c. The NiCl_4^{2-} ion is paramagnetic while the PtCl_4^{2-} ion is diamagnetic.
- d. The CoCl_4^{2-} ion is strongly colored while the ZnCl_4^{2-} ion is colorless.
- e. The MnO_4^- ion is strongly colored while the ReO_4^- ion is colorless.

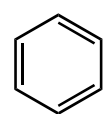
7. [12%] Consider the species whose normal boiling points are listed below.

Species	LiH	CH ₄	NH ₃	H ₂ O	HF	Ne
bp (°C)	> 900	-164	-33	100	19	-246

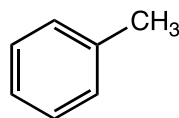
- a. Explain why LiH has a much higher boiling point than any of the other species in the table.
- b. Explain why NH₃ has a higher boiling point than CH₄.
- c. Explain why H₂O has a higher boiling point than either NH₃ or HF.
- d. Explain why CH₄ has a higher boiling point than Ne.
- e. The species BH₃ does not appear on this list because it is not a stable molecule. Draw a clear picture of the three-dimensional structure of the stable boron hydride that has the empirical formula BH₃, and predict where the boiling point of this boron hydride falls among the six species listed in the table.

8. [13%] Elemental bromine reacts with different hydrocarbons under different conditions.

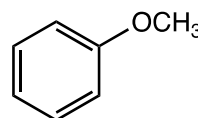
- a. Bromine reacts rapidly with cyclohexene, C₆H₁₀, at room temperature. Draw a structural formula for the major organic product of this reaction, clearly depicting stereochemistry if relevant.
- b. Bromine does not react with cyclohexane, C₆H₁₂, at room temperature in the dark, but does react in the presence of light. Draw a structural formula for the major organic product of this reaction, and clearly explain the role of light in the reaction.
- c. Bromine does not react readily with benzene, C₆H₆, in the absence of a catalyst, but in the presence of a suitable catalyst it forms bromobenzene, C₆H₅Br. Give an example of a suitable catalyst and clearly explain its role in the reaction.
- d. Under the conditions in (c), each of the benzene derivatives shown below reacts with bromine. Indicate which compound reacts the fastest and which the slowest, and explain your reasoning.



benzene



toluene



anisole

- e. In the presence of excess bromine and a catalyst as described in (c), benzene reacts to form a mixture of isomers of dibromobenzene, C₆H₄Br₂. Draw structural formulas for the three isomers that are formed and indicate which one is formed in the *smallest* quantity.

2021 USNCO Part 2 Solutions

1. a. $P = [(20.0 \text{ mm Hg})/(760 \text{ mm Hg/atm})](1.013 \text{ bar/atm}) = 0.0267 \text{ bar}$
 $n = PV/RT = (0.0267 \text{ bar})(1.00 \text{ L})/(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(512.8 \text{ K}) = 6.26 \times 10^{-4} \text{ mol}$
 $M = 0.0695 \text{ g}/6.26 \times 10^{-4} \text{ mol} = 111 \text{ g mol}^{-1}$
- b. $1.00 \text{ g}/(111 \text{ g mol}^{-1}) = 9.01 \times 10^{-3} \text{ mol}$ of the oxide
 Electrolysis requires $(58 \text{ min})(60 \text{ s/min})(1.00 \text{ A}) = 3480 \text{ C}$
 $3480 \text{ C}/(96500 \text{ C/mol}) = 0.0361 \text{ mol electrons}/9.01 \times 10^{-3} \text{ mol}$ of the oxide = 4.0
 It thus requires 4 mol electrons per mol compound to reduce $m \text{ X}$ to its elemental form, which corresponds to 2 O atoms per formula unit.
- c. If the oxide has $n = 1$, then the atomic mass of $\text{X} = (111 - 32) = 79$, $\text{X} = \text{Se}$. SeO_2 is indeed a white, slightly volatile, acidic oxide, so this is reasonable.
 If the oxide has $n = 2$, then the atomic mass of $\text{X} = 79/2 = 39.5$. This is not especially close to any atomic mass, but the closest would be K and Ca. K_2O_2 is not an oxide (it is a peroxide), and Ca_2O_2 is not plausible as a volatile molecule and would be a basic oxide, not an acidic one.
 If $n = 3$, then the atomic mass of X would be $79/3 = 26.3$. Close to Al, but Al_3O_2 is not a stable oxide, and higher values of n are even worse.
 So the oxide is **SeO₂**.
- d. $\text{Ba}^{2+}(\text{aq}) + 2 \text{OH}^{-}(\text{aq}) + \text{SeO}_2(\text{s}) \rightarrow \text{BaSeO}_3(\text{s}) + \text{H}_2\text{O}(\text{l})$
 or
 $\text{Ba}^{2+}(\text{aq}) + 2 \text{OH}^{-}(\text{aq}) + \text{H}_2\text{SeO}_3(\text{aq}) \rightarrow \text{BaSeO}_3(\text{s}) + 2 \text{H}_2\text{O}(\text{l})$
- e. In part (a), a smaller amount of SeO_2 was used, and we found the equilibrium vapor pressure at $T_1 = 512.8 \text{ K}$. Here, using more SeO_2 will require a higher temperature to achieve a higher vapor pressure so that a larger mass will fill the same volume:
 $0.4157 \text{ g SeO}_2/(111.0 \text{ g mol}^{-1}) = 3.745 \times 10^{-3} \text{ mol}$
 $P = nRT/V = (3.745 \times 10^{-3} \text{ mol})(0.08314 \text{ L bar mol}^{-1} \text{ K}^{-1})(553.2 \text{ K})/(1.00 \text{ L}) = 0.172 \text{ bar}$
 $\ln(P_2/P_1) = (-\Delta H^\circ_{\text{subl}}/R)(1/T_2 - 1/T_1)$
 $\Delta H^\circ_{\text{subl}} = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})\ln(0.172 \text{ bar}/0.0267 \text{ bar})\left([1/553.2 \text{ K}] - [1/512.8 \text{ K}]\right)^{-1}$
 $\Delta H^\circ_{\text{subl}} = 10900 \text{ J mol}^{-1} = 109 \text{ kJ mol}^{-1}$

2021 USNCO Part 2 Solutions

2. a. $\text{pH} = 12.40$, so $\text{pOH} = 14.00 - 12.40 = 1.60$, $[\text{OH}^-] = 10^{-\text{pOH}} = 0.0251 \text{ M}$

b. $[\text{Ca}^{2+}] = 0.5[\text{OH}^-] = 0.0126 \text{ M}$
 $K_{\text{sp}} = [\text{Ca}^{2+}][\text{OH}^-]^2 = [0.0126][0.0251]^2 = 7.9 \times 10^{-6}$

c. When $\text{pH} = 7.00$, the hydroxide has been exactly neutralized by the H_2SO_4 , so the number of moles of Ca^{2+} is equal to the number of moles of SO_4^{2-} present. Some of both will have precipitated as CaSO_4 , but $[\text{Ca}^{2+}]$ is still equal to $[\text{SO}_4^{2-}]$ in solution. So

$$[\text{Ca}^{2+}][\text{SO}_4^{2-}] = K_{\text{sp}}$$

$$[\text{Ca}^{2+}]^2 = 2.4 \times 10^{-5}$$

$$[\text{Ca}^{2+}] = 0.0049 \text{ M}$$

d. $0.1000 \text{ g Ca(OH)}_2 / (74.09 \text{ g mol}^{-1}) = 0.001350 \text{ mol Ca(OH)}_2$.

So if the solution becomes homogeneous, then $[\text{Ca}^{2+}] = (0.001350 \text{ mol}) / (0.100 \text{ L}) = 0.0135 \text{ M}$. (The volume change in the titration is negligible since less than 0.5 mL of the sulfuric acid solution is added to reach the endpoint.)

In order for the solid Ca(OH)_2 to have just dissolved, $[\text{Ca}^{2+}][\text{OH}^-]^2 = K_{\text{sp}}$ of Ca(OH)_2

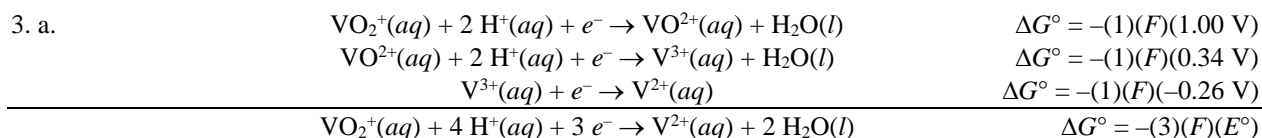
$$[0.0135][\text{OH}^-]^2 = 7.9 \times 10^{-6}$$

$$[\text{OH}^-] = 0.0242 \text{ M}$$

Since the initial number of moles of hydroxide = $2(0.001350 \text{ mol}) = 0.00270 \text{ mol}$, this means that $0.00270 \text{ mol} - 0.00242 \text{ mol} = 0.00028 \text{ mol}$ hydroxide were neutralized, requiring $0.00014 \text{ mol H}_2\text{SO}_4$ and creating $[\text{SO}_4^{2-}] = (0.00014 \text{ mol}) / (0.100 \text{ L}) = 0.0014 \text{ M}$.

So at this point, $[\text{Ca}^{2+}][\text{SO}_4^{2-}] = [0.0135][0.0014] = 1.9 \times 10^{-5}$. Since this ion product is less than the K_{sp} of CaSO_4 , CaSO_4 will not have begun to precipitate yet, and the solution **will be homogeneous** at this point.

2021 USNCO Part 2 Solutions



$$-(3)(F)(E^\circ) = -(F)(1.00 \text{ V} + 0.34 \text{ V} - 0.26 \text{ V})$$

$$E^\circ = +0.36 \text{ V}$$

b. $\Delta E^\circ = 1.00 \text{ V} - (-0.26 \text{ V}) = 1.26 \text{ V}$

c. $\Delta G^\circ = -nF\Delta E^\circ = \Delta H^\circ - T\Delta S^\circ$, so $\Delta E^\circ = (-\Delta H^\circ/nF) + T\Delta S^\circ/nF$

If ΔE° increases by $1.76 \times 10^{-4} \text{ V K}^{-1}$, then $\Delta S^\circ/nF = 1.76 \times 10^{-4} \text{ V K}^{-1}$.

$$\Delta S^\circ = (1)(96500 \text{ J V}^{-1} \text{ mol}^{-1})(1.76 \times 10^{-4} \text{ V K}^{-1}) = 17.0 \text{ J mol}^{-1} \text{ K}^{-1}$$

At 298 K, $\Delta G^\circ = -nF\Delta E^\circ = -(1)(96.5 \text{ kJ V}^{-1} \text{ mol}^{-1})(1.26 \text{ V}) = -121.6 \text{ kJ mol}^{-1}$

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

$$-121.6 \text{ kJ mol}^{-1} = \Delta H^\circ - (298 \text{ K})(0.0170 \text{ kJ mol}^{-1} \text{ K}^{-1})$$

$$\Delta H^\circ = -117 \text{ kJ mol}^{-1}$$

d. Using the Nernst equation (with base 10 logarithm, at 298 K):

$$\Delta E = \Delta E^\circ - (0.0591/n)\log\left(\frac{[\text{VO}^{2+}][\text{V}^{3+}]}{[\text{VO}_2^+][\text{V}^{2+}][\text{H}^+]^2}\right)$$

$$1.14 \text{ V} = 1.26 \text{ V} - 2(0.0591)(\text{pH}) - 0.0591\log\left(\frac{[\text{VO}^{2+}][\text{V}^{3+}]}{[\text{VO}_2^+][\text{V}^{2+}]}\right)$$

$$1.14 \text{ V} = 1.14 \text{ V} - 0.0591\log\left(\frac{[\text{VO}^{2+}][\text{V}^{3+}]}{[\text{VO}_2^+][\text{V}^{2+}]}\right)$$

$$\log\left(\frac{[\text{VO}^{2+}][\text{V}^{3+}]}{[\text{VO}_2^+][\text{V}^{2+}]}\right) = 0$$

So the numerator and denominator must be equal, which means (given the initial concentrations of 0.50 M for both vanadium reactants and 0.10 M for both vanadium products) that all vanadium species must have equal concentrations. So $[\text{V}^{3+}] = 0.30 \text{ M}$.

e. Since $[\text{V}^{3+}]$ increases by 0.20 M in a 0.100 L solution, this corresponds to the passage of $(1)(96500 \text{ C mol}^{-1})(0.20 \text{ mol L}^{-1})(0.100 \text{ L}) = 1930 \text{ C}$. At a current of 10.0 A,

$$(10.0 \text{ A})t = 1930 \text{ C}$$

$$t = 193 \text{ s}$$

2021 USNCO Part 2 Solutions

4. a. $\Delta G^\circ_{4a} = -RT \ln(K_{4a})$
 At 298 K, $\Delta G^\circ_{4a} = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(298 \text{ K}) \cdot \ln(1.12 \times 10^4) = -23.10 \text{ kJ mol}^{-1}$
 At 340 K, $\Delta G^\circ_{4a} = -(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(340 \text{ K}) \cdot \ln(4.68 \times 10^3) = -23.89 \text{ kJ mol}^{-1}$

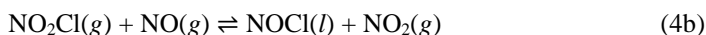
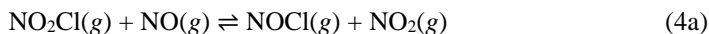
b. Since $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$:
 $\Delta H^\circ - (298 \text{ K})\Delta S^\circ = -23.10 \text{ kJ mol}^{-1}$
 $\Delta H^\circ - (340 \text{ K})\Delta S^\circ = -23.89 \text{ kJ mol}^{-1}$

Solving the simultaneous equations gives

$$\begin{aligned} \Delta H^\circ &= -17.5 \text{ kJ mol}^{-1} \\ \Delta S^\circ &= 18.8 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

c. NO(g) has the lowest molar entropy because all four compounds are in the gaseous state, but NO has the fewest atoms per molecule and hence the fewest degrees of freedom among which energy can be distributed. All other molecules have a bond between nitrogen and oxygen (like NO), but also have other bonds among which energy can be distributed.

d. The properties of reaction 4b can be determined from those of 4a plus those of the condensation reaction 4*:



$\Delta H^\circ_{4b} = \Delta H^\circ_{4a} + \Delta H^\circ_{4^*}$. Since $\Delta H^\circ_{4^*}$ is negative [condensation is exothermic],

$$\Delta H^\circ_{4b} < \Delta H^\circ_{4a}$$

$\Delta S^\circ_{4b} = \Delta S^\circ_{4a} + \Delta S^\circ_{4^*}$. Since $\Delta S^\circ_{4^*}$ is negative [liquid has a lower entropy than gas],

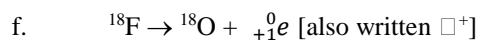
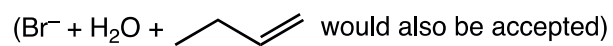
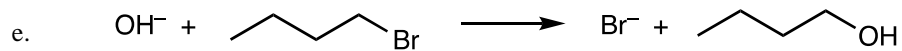
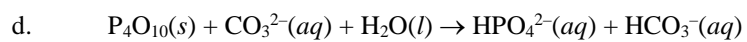
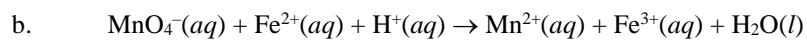
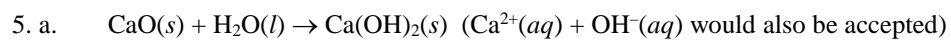
$$\Delta S^\circ_{4b} < \Delta S^\circ_{4a}$$

$\Delta G^\circ_{4b} = \Delta G^\circ_{4a} + \Delta G^\circ_{4^*}$. Since $\Delta G^\circ_{4^*}$ is positive at 298 K [at temperatures above the normal boiling point, the gas is more stable at standard pressure than the liquid],

$$\Delta G^\circ_{4b} > \Delta G^\circ_{4a}$$

e. As the volume of the container is doubled, all of the partial pressures of the gases will undergo an instantaneous decrease by a factor of two. Reaction 4a has an equal number of gaseous reactants as products, so its position will not be directly affected by this change. However, reaction 4c has more moles of reactants than products, so that reaction will shift to increase the number of moles of NO₂(g). By Le Chatelier's principle, this will shift reaction 4a to the left, so the number of moles of NOCl(g) will **decrease**.

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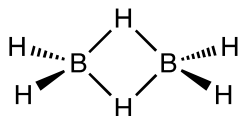


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6. a. $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ has an odd number of electrons (Cr(III) has a d^3 configuration) and thus must be paramagnetic. $\text{Sc}(\text{H}_2\text{O})_6^{3+}$ has a d^0 metal ion, so all electrons are paired, giving a diamagnetic ion.
- b. F^- is a weaker field ligand than CN^- , so the splitting between the two sets of d orbitals in an octahedral complex (the three so-called t_{2g} or $d\pi$ orbitals at lower energy and the two e_g or $d\sigma^*$ orbitals at higher energy) is lower in CoF_6^{3-} than in $\text{Co}(\text{CN})_6^{3-}$. So the six d electrons occupy all five d orbitals in CoF_6^{3-} , giving four unpaired electrons, while they are confined to the three t_{2g} orbitals in $\text{Co}(\text{CN})_6^{3-}$ and are thus all paired.
- c. NiCl_4^{2-} is tetrahedral, and so all the d orbitals are similar in energy (three are at slightly higher energy and two at slightly lower energy, but the difference in energy is small). In its ground state, the eight d electrons in Ni(II) spread out as much as possible among the five d orbitals. This means that there are two half-filled d orbitals, so the compound has 2 unpaired electrons. In square planar PtCl_4^{2-} , one d orbital ($d_{x^2-y^2}$, if the chlorides are taken to lie along the x and y axes) is much higher in energy than any of the others. That d orbital is thus empty, and filling the remaining four d orbitals with eight electrons results in no unpaired electrons.
- d. CoCl_4^{2-} has d^7 Co(II) and so has moderately intense $d-d$ transitions where electrons are promoted from filled d orbitals to half-filled d orbitals. In contrast, ZnCl_4^{2-} has a d^{10} metal center, so all the d orbitals are completely filled and no $d-d$ transitions are possible.
- e. In MnO_4^- , Mn(VII) is d^0 , so the color cannot arise from a $d-d$ transition. It must be due to a ligand-to-metal charge transfer transition (LMCT), where an electron is promoted from a nonbonding orbital on oxygen to a Mn d orbital. This is possible in ReO_4^- as well, but the transfer requires much more energy (Mn(VII) is much more oxidizing than Re(VII)) and occurs in the ultraviolet, giving rise to a colorless species.

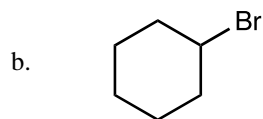
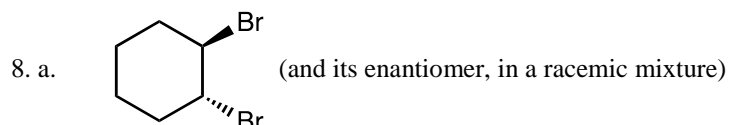
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7. a. LiH is ionic, so the cohesive forces are electrostatic interactions between Li^+ and H^- ions, which are much stronger than the intermolecular forces in the other substances, which are molecular.
- b. NH_3 can participate in hydrogen bonding, while CH_4 cannot.
- c. All three compounds can participate in intermolecular hydrogen bonding, but NH_3 and HF can only form one mole of hydrogen bonds per mole of compound (HF has only one H per mole [one H-bond donor], and NH_3 has only one lone pair [one H-bond acceptor]). Water has two H-bond donors and two H-bond acceptors per mole, so it forms twice as many hydrogen bonds and has correspondingly stronger intermolecular forces.
- d. Neither CH_4 nor Ne have permanent dipoles, nor can either participate in hydrogen bonding. The only intermolecular forces they experience are London dispersion forces. Dispersion forces are greater if the number of electrons per molecule is greater, or if the polarizability of the electrons is greater. Methane and neon each have ten electrons per molecule, but neon holds its electrons much more tightly than either carbon or hydrogen does (larger Z_{eff}) and so is much less polarizable. This means that an instantaneous dipole on one Ne atom is relatively ineffective at inducing a dipole on a neighboring Ne.



- e. B_2H_6 cannot participate in hydrogen bonding (so it is likely to have weaker intermolecular forces than NH_3) but has more electrons than CH_4 or Ne (so it will have stronger London dispersion forces). Its normal boiling point is therefore expected to fall between that of CH_4 and that of NH_3 (experimentally, it boils at $-92\text{ }^\circ\text{C}$).

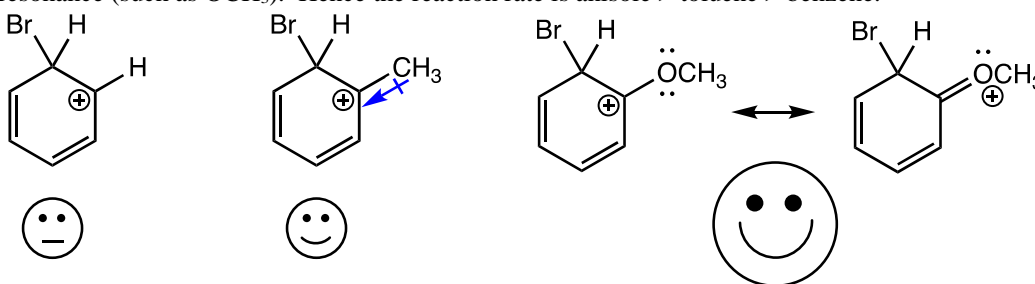
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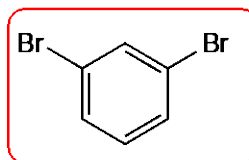
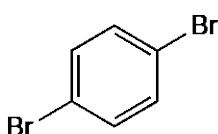
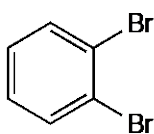
This is a radical chain reaction, and light serves to homolyze the Br–Br bond and generate the chain-carrying Br atoms.

c. Suitable catalysts are Lewis acids such as FeBr_3 or AlBr_3 , which make Br_2 a stronger electrophile.

d. The key high-energy intermediate in electrophilic aromatic substitution reactions is a cyclohexadienyl cation. This cation is stabilized (and hence the barrier to the reaction is lowered) by groups that can donate electrons inductively (such as CH_3) and very strongly stabilized by groups that can donate electrons by resonance (such as OCH_3). Hence the reaction rate is anisole > toluene > benzene.



e.



least abundant—Br is electron-donating by resonance and stabilizes the intermediates for ortho and para, but not meta, products