

THE UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
FINAL EXAMINATION
CHEMISTRY 209

Date: Saturday, December 19th, 2015

Time: 7:00pm – 10:00pm

First Name: _____

Last Name: _____

ID: _____

Please circle your lecture section:

L01 Dr. Musgrove-Richer
TR 2:00 pm

L02 Dr. Sandblom
TR 12:30 pm

This is a closed-book examination. The use of camera devices, MP3 Players and headphones, or wireless access devices such as cell phones, Blackberries, etc., during the examination will not be allowed. Only non-programmable Schulich-approved calculators are permitted. A Chemical Data Sheet is provided at the end of the exam and can be removed for quick reference.

Instructions:

All questions must be answered to obtain full points. The answers to the multiple-choice section must be entered on the optical score sheet **within** the 3 hour exam time. The answers to the long answer questions must be written in the space provided on the question sheets.

This test consists of **24 multiple choice** questions worth 2 points each (total 48 points) and **4 long answer** questions (total 42 points). The total value for the test is 90 points. The exam has **14 pages** (including this one), so please make sure you have all 14 pages.

**AT THE END OF THE EXAMINATION,
HAND IN THE OPTICAL SCORE SHEET AND THE ENTIRE EXAM PAPER.**

Failing to encode this Exam Booklet or your Optical Score Sheet correctly for your name, ID, version letter and lecture section will result in the loss of two points.

Sec II - Q1	Sec II - Q2	Sec II - Q3	Sec II - Q4
Do not write in the shaded part. For marking only.			

SECTION I – Machine-graded section (Total value 48)
To be answered on Optical Score Sheet

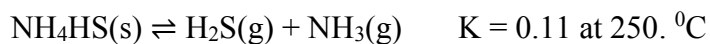
1. Two reactions both follow the form $A + B \rightarrow \text{products}$. Reaction 1 has rate constant $k = 25.6 \text{ mol L}^{-1} \text{ s}^{-1}$, while Reaction 2 has a rate constant $k = 65.2 \text{ mol L}^{-1} \text{ s}^{-1}$. If [A] and [B] are the same for both reactions, which one will have the fastest rate of disappearance of A?
 - a. Reaction 1 will have the largest rate
 - b. Reaction 2 will have the largest rate
 - c. Both reactions will have the same rate
 - d. Not enough information is given to determine the rate

2. Tetrafluoroethylene can be converted to octafluorocyclobutane and the rate constant for this process is $0.0448 \text{ L mol}^{-1} \text{ s}^{-1}$. If the starting concentration of tetrafluoroethylene is 1.0 M, how much will remain after 3.7 minutes?
 - a. $4.6 \times 10^{-1} \text{ M}$
 - b. $1.1 \times 10^{-1} \text{ M}$
 - c. $9.1 \times 10^{-2} \text{ M}$
 - d. $4.8 \times 10^{-5} \text{ M}$

3. A student in the CHEM 209 lab performed 5 replicates of a titration during class, but when they got home they realized that one of their measurements was noticeably larger than the other 4. What is the **best** way that the student should handle this measurement while writing up their lab report?
 - a. Keep the data point because no known experimental error was made.
 - b. Discard the data point if it is obviously different from the rest.
 - c. Discard the data point only if it is more than one standard deviation from the average value.
 - d. Discard the data point only if $G_{\text{calc}} > G_{\text{table}}$ in the Grubbs test.

Use this information to answer questions 4-6.

Ammonium hydrogen sulfide decomposes according to this endothermic reaction ($\Delta H = 93 \text{ kJ mol}^{-1}$):



$$K_a \text{ of H}_2\text{S is } 1.0 \times 10^{-7}$$

$$K_b \text{ of NH}_3 \text{ is } 1.8 \times 10^{-5}$$

4. Predict, if possible, what will happen if a mixture contains 1.0 bar of each of hydrogen sulfide (H_2S) and ammonia (NH_3).
- Ammonium hydrogen sulfide will be formed.
 - Ammonium hydrogen sulfide will be consumed.
 - The amount of ammonium hydrogen sulfide needs to be specified.
 - The volume of the container needs to be specified.
5. Determine K at $512 \text{ } ^\circ\text{C}$.
- 1.1×10^{-1}
 - 2.3×10^{-1}
 - 1.4×10^2
 - 9.7×10^8
6. Calculate K_c for the reaction:
- $$\text{NH}_4^+(\text{aq}) + \text{HS}^-(\text{aq}) \rightleftharpoons \text{H}_2\text{S(aq)} + \text{NH}_3(\text{aq})$$
- 1.8×10^{-12}
 - 5.5×10^{-3}
 - 1.8×10^{-5}
 - 5.5×10^{11}

7. Calculate K_a for an unknown acid if a 0.0100 M solution has a measured pH of 2.60.
- 2.5×10^{-1}
 - 6.3×10^{-4}
 - 8.4×10^{-4}
 - 6.3×10^{-6}

8. The rate law for the overall reaction $A + 2B \rightarrow E$ was experimentally determined to be:

$$\text{Rate} = k[A]^2[B]$$

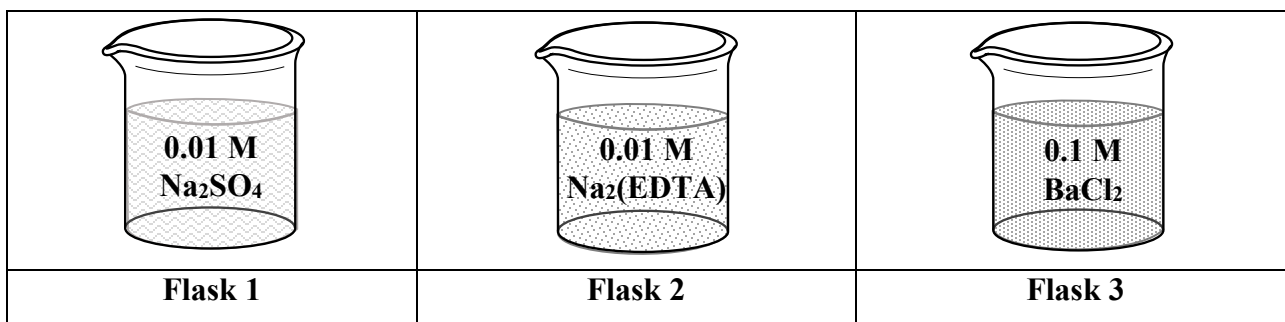
Which of these proposed mechanisms could explain this observed rate law?

- Step 1 (slow): $A_2 + B \rightarrow C$
Step 2 (fast): $C + B \rightarrow E$
 - Step 1 (slow): $2A + B \rightarrow C$
Step 2 (fast): $C + B \rightarrow E$
 - Step 1 (slow): $A + B \rightarrow C$
Step 2 (fast): $C + B \rightarrow E$
 - Step 1 (slow): $2A + B \rightarrow C$
Step 2 (fast): $C + B \rightarrow E + A$
9. The potentiometric endpoint for the titration of 25.00 mL of acetic acid is 23.03 mL. If K_a of acetic acid is 1.8×10^{-5} and the base used in the titration is 0.012 M NaOH, calculate the acid concentration.
- $8.3 \times 10^{-5} \text{ M}$
 - $1.1 \times 10^{-2} \text{ M}$
 - $1.2 \times 10^{-2} \text{ M}$
 - $1.1 \times 10^1 \text{ M}$

10. Copper(II) chromate (CuCrO_4) is partially soluble in water. A solution of 0.030 M CuBr_2 is titrated with $0.10 \text{ M Na}_2\text{CrO}_4$ until the chromate concentration in solution is $1.2 \times 10^{-4} \text{ M}$, at which point a precipitate appears. What is the K_{sp} for copper chromate?

- 3.6×10^{-6}
- 9.0×10^{-6}
- 3.0×10^{-4}
- 1.4×10^{-8}

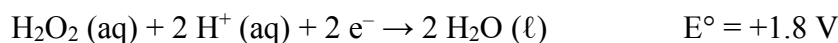
11. A student adds some BaSO_4 to each of the three flasks shown here.



Given that BaSO_4 has $K_{\text{sp}} = 1.3 \times 10^{-10}$ and $\text{Ba}(\text{EDTA})^{2-}$ has $K_{\text{f}} = 7.2 \times 10^7$, which choice below correctly ranks the solubility of BaSO_4 in these flasks?

	Highest BaSO_4 Solubility		Lowest Solubility
a.	Flask 1	Flask 2	Flask 3
b.	Flask 3	Flask 2	Flask 1
c.	Flask 2	Flask 1	Flask 3
d.	Flask 2	Flask 3	Flask 1

12. The standard potentials for two half-reactions are shown below. Based on this information, which species is the **stronger oxidizing agent**?



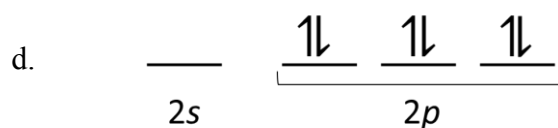
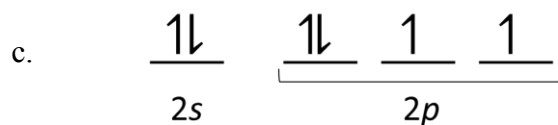
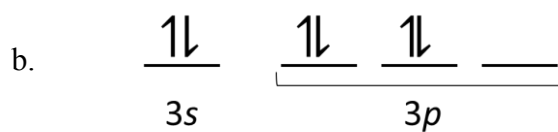
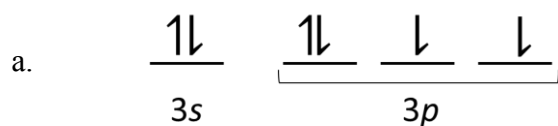
- $\text{Cl}_2 (\text{g})$
- $\text{Cl}^- (\text{aq})$
- $\text{H}_2\text{O}_2 (\text{aq})$
- $\text{H}_2\text{O} (\ell)$

13. Which of the choices below correctly shows the balanced equation for the reaction of Zn and vanadium oxide (VO_2^+) in acidic solution, forming Zn^{2+} and VO^{2+} ?
- $\text{Zn (s)} + 2 \text{H}^+ \text{(aq)} + \text{VO}_2^+ \text{(aq)} \rightarrow \text{Zn}^{2+} \text{(aq)} + \text{VO}^{2+} \text{(aq)} + \text{H}_2\text{O (l)}$
 - $\text{Zn (s)} + 4 \text{H}^+ \text{(aq)} + 2 \text{VO}_2^+ \text{(aq)} \rightarrow \text{Zn}^{2+} \text{(aq)} + 2 \text{VO}^{2+} \text{(aq)} + 2 \text{H}_2\text{O (l)}$
 - $\text{Zn (s)} + 2 \text{H}_2\text{O (l)} + 2 \text{VO}_2^+ \text{(aq)} \rightarrow \text{Zn}^{2+} \text{(aq)} + 2 \text{VO}^{2+} \text{(aq)} + 4 \text{OH}^- \text{(aq)}$
 - $\text{Zn (s)} + \text{H}^+ \text{(aq)} + \text{VO}_2^+ \text{(aq)} \rightarrow \text{Zn}^{2+} \text{(aq)} + \text{VO}^{2+} \text{(aq)} + \text{OH}^- \text{(aq)}$
14. The E° for the reaction of Cu/Cu^{2+} and Sn/Sn^{2+} is + 0.19 V. What is the value of the equilibrium constant K for this reaction at 298 K?
- 3.7×10^{-7}
 - 1.6×10^4
 - 2.7×10^6
 - 6.2×10^{14}

This question's content was not covered this year.

16. Select the **true** statement.
- The d subshell has 10 orbitals.
 - The 4s orbital has 4 nodes.
 - The 6p orbitals have 6 possible orientations.
 - The 5f orbitals are degenerate.
17. Which of these elements should have the largest **first** ionization energy?
- O
 - F
 - Na
 - Cl

19. Which of the following orbital diagrams correctly shows the ground-state valence electron configuration for a S atom?

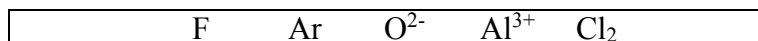


20. Consider the atomic and ionic radii shown in the table below. Which atomic property **best** explains the trend in these radii?

Species	Radius (pm)
Br ⁻	182
Rb ⁺	166

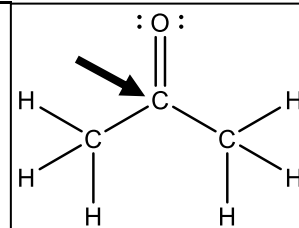
- Principal quantum number n
- Effective nuclear charge
- Partially filled subshells
- Atomic mass

21. Which of the following answers correctly shows the ground-state electron configuration for an As^+ ion?
- $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^2$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^3$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{14} 4p^2$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^3$
22. How many chemical species in this list are diamagnetic in their ground state?



- One
- Two
- Three
- Four

Acetone is a powerful solvent used in the lab, and occasionally in the household as a nail polish remover. Use the chemical structure of acetone, shown here, to help you answer the following two questions.



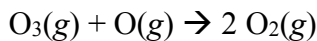
23. What is the hybridization on the carbon atom marked with an arrow?
- sp
 - sp^2
 - sp^3
 - unhybridized
24. Which statement below is **true** with regards to the bonding in the acetone molecule?
- There are two pi bonds in the molecule.
 - There are ten sigma bonds in the molecule.
 - All of the bonds on the atom indicated with an arrow on the structure above are nonpolar bonds.
 - The atom indicated with an arrow in the structure above has one pi bond and three sigma bonds.

*******END OF MULTIPLE CHOICE*******

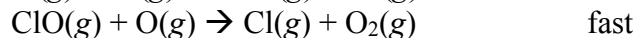
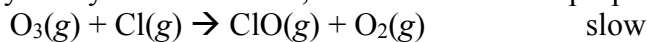
SECTION II: Long Answers: To be graded manually (Total value 42)
For full marks show all your work.

Question 1 [Total: 8 points]

Ozone reacts with oxygen atoms to make oxygen gas as an exothermic process that occurs as a single elementary step:



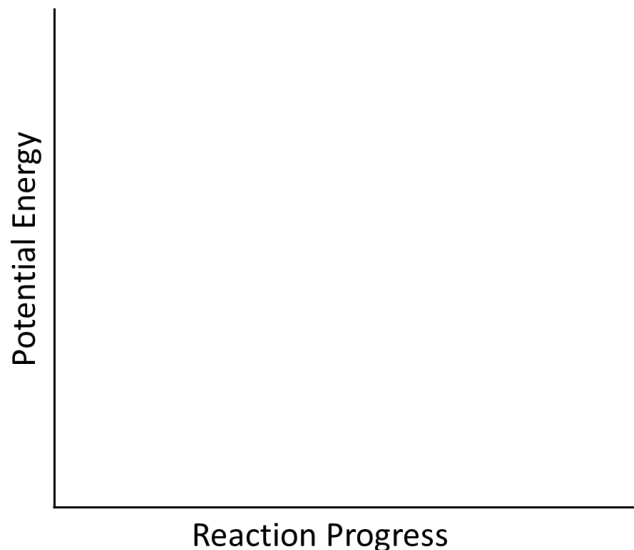
This reaction can also be catalyzed by chlorine atoms, as described in this proposed reaction mechanism:



a. [1 point] Write the rate law for the uncatalyzed reaction.	
b. [1 point] Write the rate law for the catalyzed reaction.	
c. [1 point] How many transition states would you expect for the catalyzed reaction?	
d. [1 point] How would you describe the chlorine atoms? (Check one box)	<input type="checkbox"/> Homogeneous catalyst <input type="checkbox"/> Heterogeneous catalyst

e. [3 points] Draw a potential energy diagram for the uncatalyzed reaction, including labels for:

- Reactants (“R”)
- Products (“P”)
- For the forward reaction:
 - Activation Energy (E_a^{Uncat}) for the rate determining step
 - ΔH



f. The bond length is 128 pm in O_3 and 110 pm in O_2 . Which bond would be stronger? Explain your answer in 1-3 grammatically correct sentences. [1 mark]

Question 2 [Total: 10 Points]

You prepare a 0.50 M solution of bromous acid (HBrO_2). Bromous acid has $\text{p}K_a = 3.43$

- a. [3 points] What is the pH of this solution?
- b. [3 points] How many L of 0.48 M NaOH would you need to add to 50.0 L of this acid to make a buffer with $\text{pH} = 4.00$?
- c. [2 points] Draw one Lewis diagram for the conjugate base, BrO_2^- , and show formal charge calculations for each atom to prove that it is the best Lewis structure for this compound.

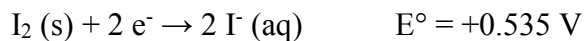
Lewis structure:

- d. [2 points] Based on your conjugate base Lewis diagram, draw the VSEPR structure for the acid, HBrO_2 .

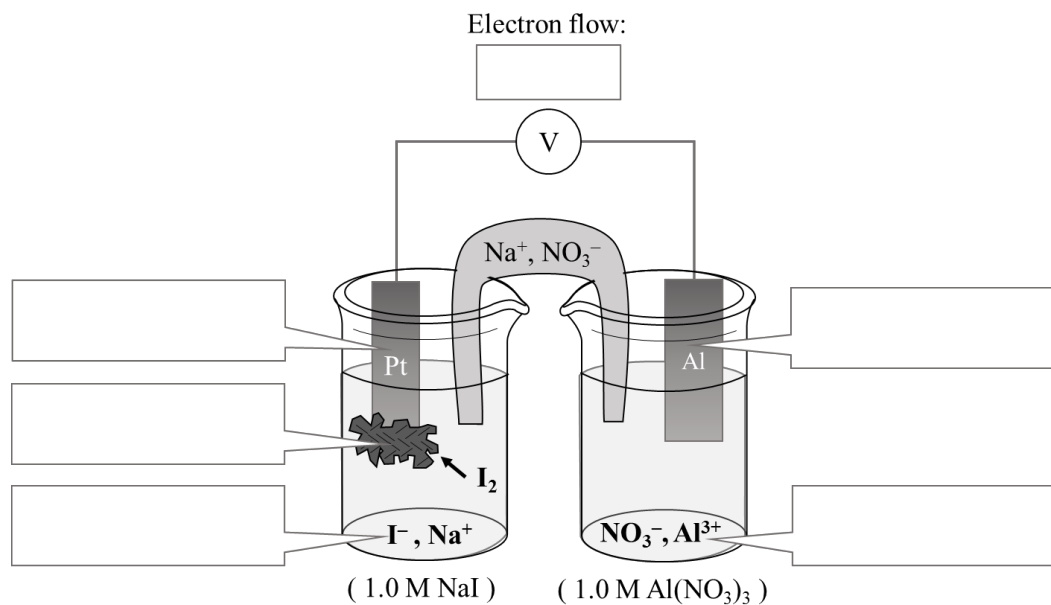
Lewis structure:

Question 3 [Total: 10 points]

The cell below is a voltaic cell based on the reaction between Al/Al^{3+} and I_2/I^- . Use this diagram and the standard reduction potentials given to answer Question 3.



- a. [2 points] Label the indicated cell parts using the following terms: **Cathode**, **Species Being Reduced**, and **Species Being Oxidized**. As well, use the space provided to indicate the **direction of electron flow**.



- b. [1 point] Write the balanced redox equation for the reaction of aluminum and iodine (as seen in this cell), in acidic solution.

- c. [1 point] Assuming that the voltmeter is connected correctly, what reading should it display?

- d. [1 point] Write the full electron configuration for the neutral aluminum atom:

- e. [1 point] Arrange the redox-active atoms & ions from this reaction (Al , Al^{3+} and I^-) in order of INCREASING size Write your answers in the unshaded boxes.

SMALLEST

LARGEST

f. [4 points] If the solution in the two cell compartments was replaced with the solutions described in the table below, what reading would the voltmeter then display?

	Components
In left-hand beaker (I_2 / I^-):	10.2 g of KI in 250. mL of water
In right-hand beaker (Al / Al^{3+}):	23.1 g of $Al(NO_3)_3$ in 250. mL of water

Question 4 [Total: 14 points]

For the species given below, draw Lewis (2D) and VSEPR (3D) structures and identify electron pair arrangement, molecular shape, and net polarity. Enter your answers in the appropriate boxes.

	BF_3	KrF_4	IF_4^+	SnH_4
Lewis structure (2D) [1 point each] <i>Show all electron groups and all non-zero formal charges.</i>				
VSEPR structure (3D) [1 point each]				
Electron pair arrangement [0.5 point each]				
Molecular shape [0.5 point each]				
Check one box [0.5 point each]	<input type="checkbox"/> Polar <input type="checkbox"/> Non-polar	<input type="checkbox"/> Polar <input type="checkbox"/> Non-polar	<input type="checkbox"/> Polar <input type="checkbox"/> Non-polar	<input type="checkbox"/> Polar <input type="checkbox"/> Non-polar

*****END OF LONG ANSWER*****

Data Sheet – CHEM 209**Periodic Table**

1 1A																	18 8A
1 H 1.008	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 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 65.38	31 Ga 69.72	32 Ge 72.59	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 183.9	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 226.0	89** Ac (227)	104 Rf (261)	105 Ha (262)	106 Sg (263)	107 Ns (262)	108 Hs (265)	109 Mt (266)	110 Uun (269)	111 Uuu (272)							

Legend:

1	← Atomic number (Z)
H	← Atomic symbol
1.008	← Atomic mass (amu)

Lanthanides *

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
Actinides **													
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	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 (260)

Strong Acids: HCl, HBr, HI, HNO₃, H₂SO₄, HClO₄

Strong Bases: Hydroxides of Group 1 (Li to Cs) and Group 2 (Ca, Sr, Ba)

Constants: Gas Constant: $R = 0.08205 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ $= 8.314 \text{ L}\cdot\text{kPa}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = 8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ $= 0.08314 \text{ L}\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ Avogadro's number: $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$ Faraday's Constant: $F = 96485 \text{ C/mol electrons}$ Planck's Constant: $h = 6.626 \times 10^{-34} \text{ J}\cdot\text{s}$ Speed of Light: $c = 2.998 \times 10^8 \text{ m}\cdot\text{s}^{-1}$ Rydberg Constant: $R = 1.096776 \times 10^7 \text{ m}^{-1}$ Factoring Rydberg Constant: $R_H = R \cdot h \cdot c = 2.18 \times 10^{-18} \text{ J}$	Conversion Factors: $1 \text{ J} = 1 \text{ kg}\cdot\text{m}^2\cdot\text{s}^{-2}$ $T(\text{K}) = T(^{\circ}\text{C}) + 273.15$ $1 \text{ Pa} = 1 \text{ kg}\cdot\text{m}^{-1}\cdot\text{s}^{-2} = 10^{-5} \text{ bar}$ $1 \text{ L}\cdot\text{atm} = 101.3 \text{ J}$ $1 \text{ atm} = 760.0 \text{ torr} = 101.3 \text{ kPa} = 760.0 \text{ mm Hg} = 1.013 \text{ bar}$ $1 \text{ L} = 10^{-3} \text{ m}^3$ $1 \text{ C} = 1 \text{ J/V} \quad 1 \text{ A} = 1 \text{ C/s}$ STP conditions: 0°C, 100 kPa Electrochemical standard state: 100 kPa, 1 M, 25°C
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$$[A]_t = -kt + [A]_0$$

$$\ln[A]_t = -kt + \ln[A]_0$$

$$PV = nRT$$

$$E^{\circ} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$c = \lambda\nu$$

$$\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$K = K_C(RT)^{\Delta n}$$

$$E = E^{\circ} - \frac{0.0592}{n_e} \log Q$$

$$E = hc$$

$$E = mc^2$$

$$t_{1/2} = \frac{[A]_0}{2k}$$

$$t_{1/2} = \frac{0.693}{k}$$

$$K_w = K_a \cdot K_b$$

$$E^{\circ} = \frac{RT}{zF} \ln K$$

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

$$ax^2 + bx + c = 0$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

$$k = Ae^{(-E_a/RT)}$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$E^{\circ} = \frac{0.0592}{n_e} \log K$$

$$\Delta E = -R_H \left(\frac{Z^2}{n_f^2} - \frac{Z^2}{n_i^2} \right)$$

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

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$pH = pK_a + \log\left(\frac{[\text{base}]}{[\text{acid}]}\right)$$

$$nFE^{\circ} = RT \ln K$$