Final Exam Key   **5.111**

Write your name and your TA's name below. **Do not open the exam until the start of the exam is announced.** 1) Read each part of a problem thoroughly. Many of a problem's latter parts can be solved without having solved earlier parts. If you need a numerical result that you were not successful in obtaining for the execution of a latter part, make a physically reasonable approximation for that quantity. 2) Significant figure usage and units must be correct. 3) If you don't understand what the problem is requesting, raise your hand. 4) Physical constants, formulas and a periodic table are given on the last 2 pages. You may detach these pages **once the exam has started**.

PAGE 2	1. KINETICS & EQUILIBRIUM	(29 points)
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TOTAL   (200 points) _____

TA _____   Name _____

1. KINETICS AND EQUILIBRIUM (29 points total)

For a reversible, one step reaction $2A \rightleftharpoons B + C$, the rate constant for the forward reaction is $406 \text{ M}^{-1} \text{ min}^{-1}$ and the rate constant for the reverse reaction is $244 \text{ M}^{-1} \text{ min}^{-1}$. The activation energy for the forward reaction is 26.2 kJ mol^{-1} and that for the reverse reaction is 42.4 kJ mol^{-1}.

(a) (5 points) On the axes below, <u>draw</u> a reaction coordinate diagram for this reaction, <u>showing</u> the curve, and <u>labeling</u> **(i)** ΔE, **(ii)** $E_{a,f}$, and **(iii)** $E_{a,r}$. <u>State</u> whether the reaction is endothermic or exothermic.

reaction coordinate →
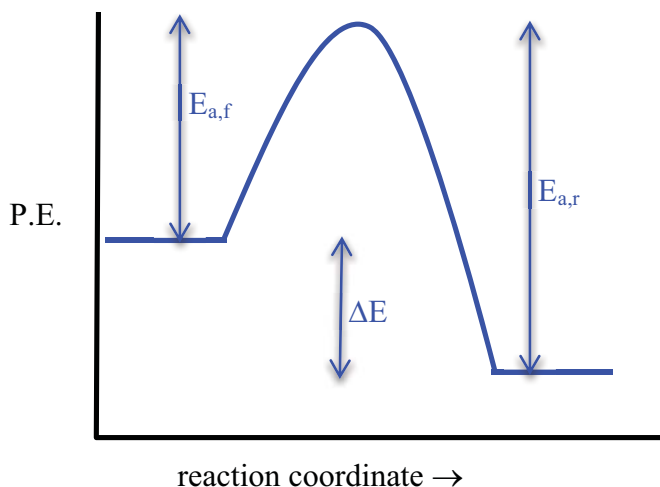
(b) (4 points) <u>Calculate</u> ΔE for this reaction ($2A \rightleftharpoons B + C$). Show your work.

-16.2 kJ/mol

(c) (4 points) <u>Calculate</u> the equilibrium constant (K) for this reaction ($2A \rightleftharpoons B + C$). Show your work.

$K = \mathbf{1.66}$

(d) (6 points) **(i)** <u>Predict</u> the effect of raising the temperature on the forward **rate constant** (k_1), and **(ii)** <u>compare</u> it to the effect of raising the temperature on the **reverse rate constant** (k_{-1}). <u>Explain your answer</u>.

Both k's will increase because more molecules will have the energy necessary to overcome the Ea barriers. $k_{reverse}$ (k_{-1}) will increase more because the Ea,r barrier is higher.

(e) (4 points) <u>Predict</u> the effect of raising the temperature on the **equilibrium constant** (K). <u>Explain your answer.</u>

K will decrease.

Le Chatelier's ~ for exothermic reaction, shift to reactant (absorb heat)

OR

K will decrease since k_{-1} (reverse) increases more than k_1 (forward) and K = $\dfrac{k1}{k\text{-}1}$

(f) (6 points) On the axes below, <u>draw</u> a single reaction coordinate diagram, that includes both a catalyzed (**dashed line**) and a noncatalyzed (**solid line**) reaction curve, indicating the effect of adding a catalyst to the reaction. <u>Briefly explain</u> what a catalyst does.

P.E.

reaction coordinate →
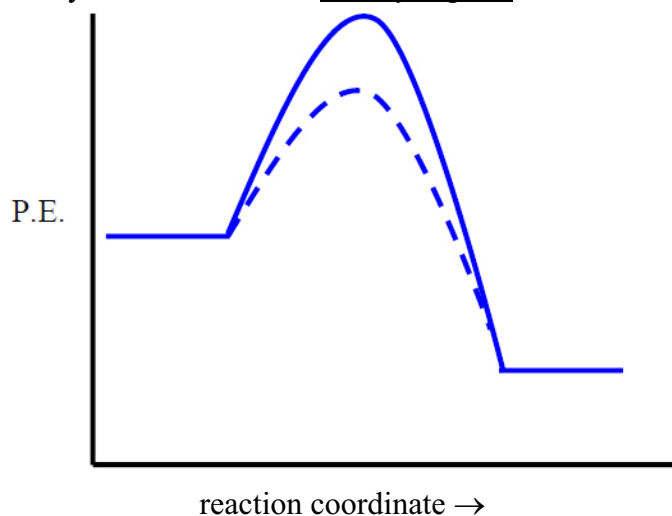
2. ENZYME KINETICS (7 points total)
The enzyme penicillinase degrades the antibiotic penicillin, leading to bacterial resistance. The Michaelis-Menten constants for this enzyme and substrate are $K_m = 5 \times 10^{-5}$ mol/L and $k_2 = 2 \times 10^3$ s^{-1}.

(a) (4 points) <u>Calculate</u> the maximum rate of this reaction if the total enzyme concentration is 7×10^{-5} M.

$V_{max} = $ **1×10^{-1} M/s**

(b) (3 points) <u>Find</u> the substrate concentration for which the rate will be half of that calculated in part (a). No need to show work.

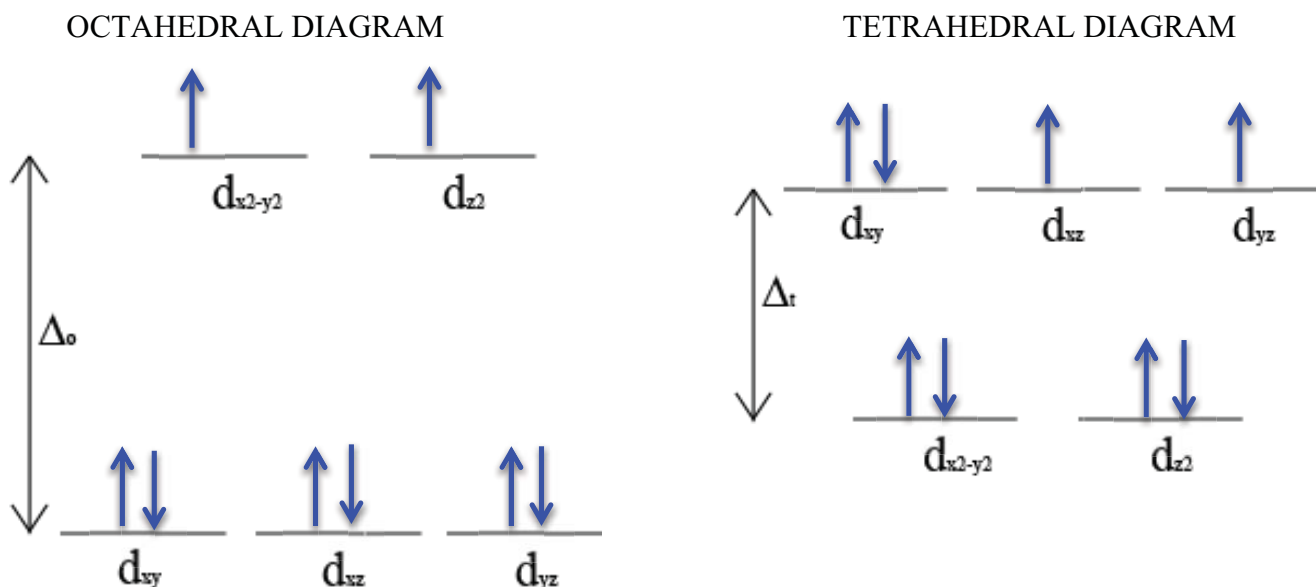**5×10^{-5} M**

3. REACTION MECHANISMS (8 points total)

For the reaction 2 NO + O_2 → 2 NO_2, <u>write</u> the rate law for the formation of NO_2 using the following mechanistic proposal and the steady state approximation. Be sure to eliminate intermediates from the rate expression. **<u>Do not</u>** make any assumptions about fast or slow steps (i.e. do not simplify your expression by assuming anything about the relative magnitude of k_{-1} and k_2). Show all work for full credit.

Step 1
$$NO + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_2$$

Step 2
$$N_2O_2 + O_2 \overset{k_2}{\rightarrow} 2\ NO_2$$
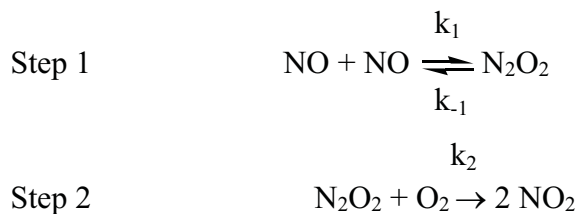
$$rate = \frac{2k_1k_2[NO]^2[O_2]}{k_{-1} + k_2[O_2]}$$

4. TRANSITION METALS (16 points total)

Ni^{2+} in a coordination complex is paramagnetic. **(a)** <u>Draw</u> the crystal field splitting diagrams <u>showing relative splitting energies</u> for an octahedral crystal field and a tetrahedral crystal field, <u>labeling</u> the diagrams with the **(b)** names of the d-orbitals, and **(c)** and symbols for octahedral and tetrahedral field splitting energy. **(e)** <u>Fill</u> both diagrams with the proper number of electrons and <u>state</u> below each diagram whether the geometry is consistent with a paramagnetic species.

OCTAHEDRAL DIAGRAM   TETRAHEDRAL DIAGRAM

d_{x2-y2} d_{z2}

Δ_o

d_{xy} d_{xz} d_{yz}

Δ_t

d_{xy} d_{xz} d_{yz}

d_{x2-y2} d_{z2}

Both are paramagnetic

5. OXIDATION-REDUCTION (8 points total)

When a ruthenium chloride solution was electrolyzed for 32 minutes with a 60-mA current, 40. mg of ruthenium was deposited. <u>Calculate</u> the oxidation number of Ru in the ruthenium chloride solution.

3 or +3 or Ru^{3+}

6. REDOX AND THERMODYNAMICS (12 points total)
Given that the standard reduction potentials for vitamin B_{12} and the protein flavodoxin are

Vitamin B_{12} $E° = -0.526$ V
Flavodoxin $E° = -0.230$ V

(a) (8 points) Calculate $\Delta G°$ **in kJ** for the one-electron reduction of vitamin B_{12} by flavodoxin.

ΔG = **28.6 kJ or kJ/mol** $_{OR}$ **28.5 kJ or kJ/mol**

(b) (4 points) State whether vitamin B_{12} or flavodoxin is the better reducing agent. Explain your answer.

Vitamin B_{12} ΔG is positive for the reduction of B_{12} by flavodoxin (non-spontaneous) which means B_{12} is the better reducing agent

OR

Vitamin B_{12} has a more negative potential, so it likes to be oxidized, thus it's a better reducing agent.

7. ACID-BASE EQUILIBRIA (10 points total)

Ketoacidosis is a serious medical condition caused by a build-up of ketone bodies. A 0.50 M solution of one of those ketone bodies, acetoacetic acid, is found to have a pH of 1.95. Determine the K_a of acetoacetic acid. Show all work.

$K_a = 2.6 \times 10^{-4}$

8. ACID-BASE TITRATION CURVES (5 points total)

On the axes below, draw a titration curve for a weak acid/strong base titration. **(a)** Mark the equivalence point, **(b)** mark the half-equivalence point, **(c)** mark the buffering region with a double headed arrow, and **(d)** indicate whether the pH at the equivalence point should be < 7, 7, or > 7.

pH

•Equivalence point, pH > 7

buffer

Half eq. pt.

Volume of strong base →
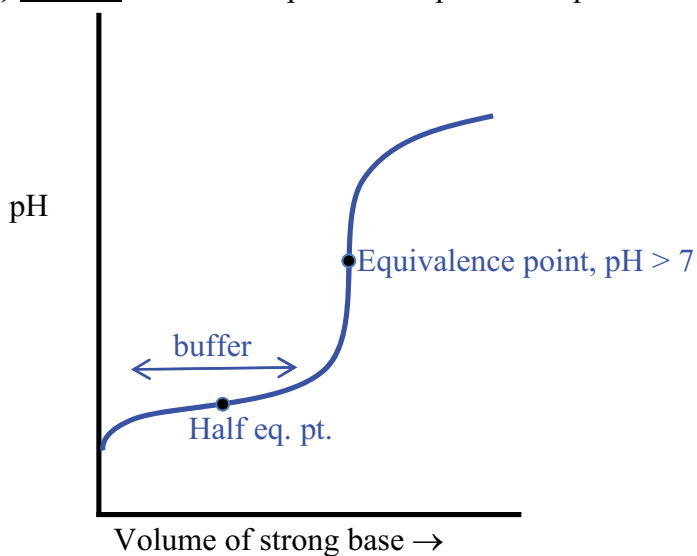
9. BUFFERS (10 points total)

Your UROP supervisor wants you to make a buffer solution with an equal number of moles of acetic acid (CH_3COOH) and acetate (CH_3COO^-). <u>Calculate</u> to **one significant figure** the minimum number of **moles** of each that you must use to prevent a change in the pH of more than 0.20 pH units after the addition of 1.0 mL of 5.00 M HCl (aq) to 100.0 mL of the buffer solution, generating 101.0 mL of solution. The K_a of acetic acid is 1.8×10^{-5}.

0.02 mol of each

10. THERMODYNAMICS (12 points total)
Without doing any calculations, predict the answers to the following questions for this reaction:
$$Cl_2 \text{ (g)} \rightarrow 2 \text{ Cl (g)}$$
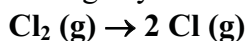
(a) (4 points) <u>Predict</u> if $\Delta H°$ for this reaction is endothermic, exothermic, or zero. <u>Explain your answer</u>.

Endothermic heat taken in to break bonds
                    OR
                Cl_2 is most stable elemental state

(b) (4 points) <u>Predict</u> if $\Delta S°$ is positive, negative, or zero. <u>Explain your answer</u>.

Positive   1 mol → 2 mol of gas

(c) (4 points) <u>Predict</u> whether this reaction is spontaneous at all temperatures. <u>Explain your answer</u>.

No, it is not. Only at T where $T\Delta S > \Delta H$
                    or
                at high temperatures only
 $\Delta G = \Delta H - T\Delta S$

11. MOLECULAR ORBITAL THEORY (26 points total)
(a) (4 points) **(i)** <u>Briefly compare</u> in words or pictures the probability density (ψ^2) between two nuclei for a σ orbital with that of a σ* orbital. **(ii)** <u>Explain</u> how this difference in probability density relates to the relative energies of electrons in these two types of molecular orbitals.
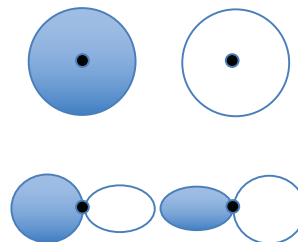
(i) Ψ^2 is high between nuclei in σ orbital (constructive interference). Destructive interference creates a nodal plane between nuclei for σ* (no Ψ^2 density)

(ii)   σ is lower in E than σ* because electrons in σ have high probability of being right between the nuclei where they are strongly bound. In σ*, no probability of being in this sweet (tightly bound) spot.
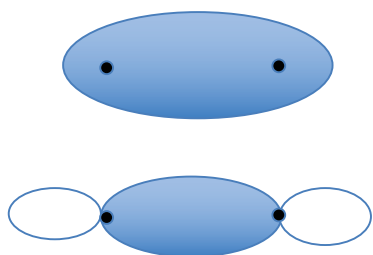
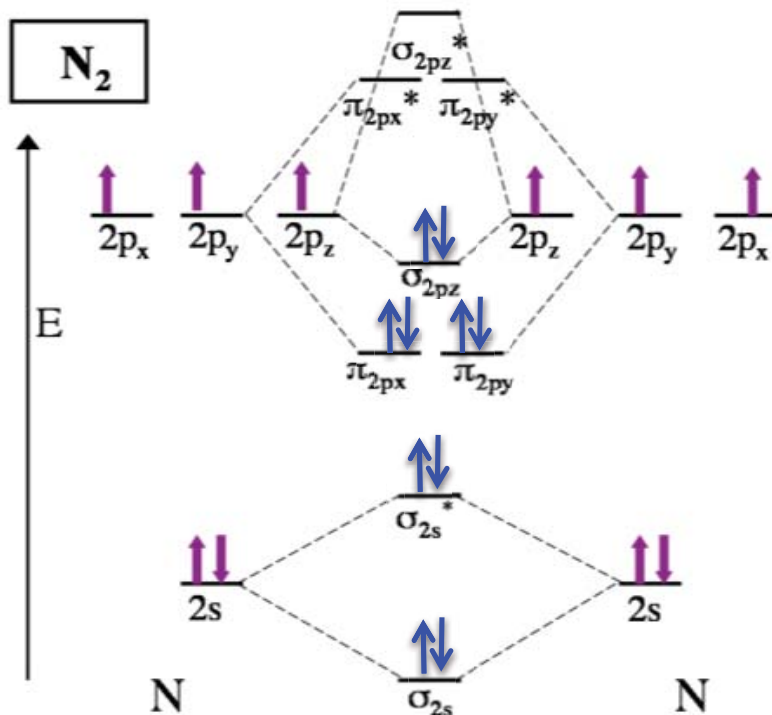**sigma**   **sigma***

(b) (10 points) **(i)** Draw the MO diagram for the **valence electrons of N_2**. Label the **(ii)** atomic and **(iii)** molecular orbitals, including the x, y, and z designations where appropriate. **(iii)** Fill both the atomic and molecular orbitals with the proper number of electrons. **(iv)** Draw and label the Energy axis. Use the full space available to spread out your energy levels.
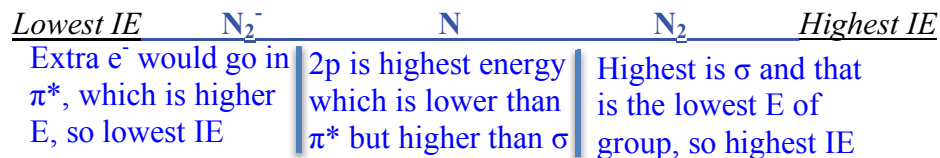

(c) (3 points) Write the valence electron configuration for N_2 from the MO diagram above.

$(\sigma_{2s})^2 \, (\sigma_{2s}{}^*)^2 \, (\pi_{2px})^2 \, (\pi_{2py})^2 \, (\sigma_{2pz})^2$

(d) (3 points) Calculate the bond order for N_2 based on the MO diagram above.

    3

(e) (6 points) **(i)** Arrange the following from lowest to highest ionization energy: N, N_2, N_2^-

| Lowest IE	N_2^-	N	N_2	Highest IE
	Extra e⁻ would go in π^*, which is higher E, so lowest IE	2p is highest energy which is lower than π^* but higher than σ	Highest is σ and that is the lowest E of group, so highest IE	

(ii) Explain your order:

Orbitals with highest E have lowest IE
          OR
N_2^- then N then N_2 is order of orbital energy from highest to lowest

12. LEWIS STRUCTURES, VSEPR, and HYDRIBIZATION (25 points total)
(a) For SF₄ (11 points)
(i) (4 points) <u>Draw</u> the most stable Lewis structure for SF₄ including lone pairs. <u>Indicate</u> any non-zero formal charge(s) and <u>draw</u> any resonance structures if appropriate.
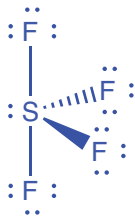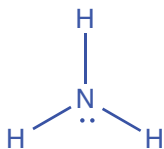
(ii) (3 points) SN is _____5_____.

(iii) (2 points) The geometry of the molecule is _____see-saw_____(example: linear).

(iv) (2 points) Circle the expected F-S-F angle or angles

<90°;   90°;   >90;   <109.5°; 109.5°; >109.5°; <120°; 120°; >120°

(b) For NH₃ (14 points)
(i) (4 points) <u>Draw</u> the most stable Lewis structure for NH₃ including lone pairs. <u>Indicate</u> any non-zero formal charge(s) and <u>draw</u> any resonance structures if appropriate.

(ii) (2 points) The geometry of the molecule is _____trigonal pyramidal_____ (example: linear)

(iii) (2 points) Circle the expected H-N-H angle or angles:

<90°;   90°;   >90;   <109.5°; 109.5°; >109.5°; <120°; 120°; >120°

(iv) (6 points) <u>Write</u> the symmetry of an N-H bond (example σ), give the hybrid or atomic orbital (with their principle quantum numbers) that overlap to form each bond. Where appropriate, include the x,y,z designations.

σ (N2sp³, H1s)

13. ORBITALS AND PERIODIC TRENDS (12 points total)
Circle the correct italicized answer and briefly explain your choice.

(a) A 1s orbital of a multi-electron atom is $\boxed{lower}$ *higher* in energy than the 1s orbital of hydrogen.
Explanation:

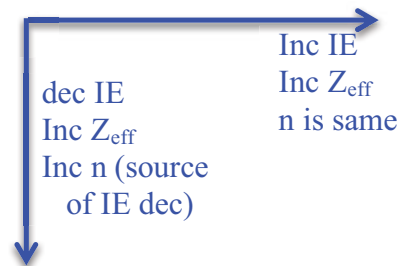High Z, electrons more tightly bound in multi-electron atom

(b) In general, ionization energy *increases* $\boxed{decreases}$ down a column of the periodic table.
Explanation:

N is bigger, electrons are farther out and easier to pull off (ionize)   OR
                              OR
Outer electrons are more shielded from pull of nucleus

dec IE
Inc Z_{eff}
Inc n (source
   of IE dec)

Inc IE
Inc Z_{eff}
n is same

(c) Low electronegativity is associated with low electron affinity and   *high* $\boxed{low}$ ionization energy.
Explanation:

Low electronegative elements want to donate e⁻, so they have low electron affinity +they have low IE.
Easier to donate e⁻ with low IE
                              OR
If it doesn't want an e⁻ (low electronegativity), then it's more likely to lose one

14. PHOTOELECTRIC EFFECT (12 points total)
Explain the following observations.

(a) (4 points) Classical physics predicted that the number of electrons ejected from a metal surface would be unaffected by increasing the intensity of the light. However, experiment showed that an increased number of electrons were ejected as the intensity of light was increased. Explain this experimental observation.

Intensity is photons per second, more intensity, more electrons

(b) (4 points) Classical physics predicted that the kinetic energy of electrons ejected from a metal surface would increase as the intensity of light increased. However, experiment showed that the kinetic energy of the electrons did not change as the intensity of light was increased. **(i)** Identify a property of light that was found by experiment to affect the kinetic energy of the ejected electrons and **(ii)** briefly explain why this property has such an effect.

ν or λ or E of electron. Intensity is number of photons per second. Only increasing the energy per photon affects the KE of the ejected electron.

(c) (4 points) Explain what threshold frequency is and why the value is dependent on the metal in question.

Threshold ν is the minimum frequency of light needed for ejection of an electron.

It depends on the metal because different metals bind the electrons with different tightness.
                                                    OR
Metals have different work function values.

15. PHOTON EMISSION (8 points total)
A new prototype UV light source emits photons at a wavelength of 388.65 nm.

(**a**) (4 points) <u>Calculate</u> the energy per photon in **Joules** to **four significant figures**.

$E = \mathbf{5.111 \times 10^{-19}}\,\boldsymbol{J}$

(**b**) (4 points) <u>Calculate</u> the total energy (in **kJ** to **three significant figures)** associated with the emission of 0.0166 moles of photons at this wavelength.

$\mathbf{5.11}\,\boldsymbol{kJ}$

$c = 2.9979 \times 10^8$ m/s

$h = 6.6261 \times 10^{-34}$ J s

$N_A = 6.02214 \times 10^{23}$ mol^{-1}

1 amu $= 1.66054 \times 10^{-27}$ kg

$m_e = 9.10939 \times 10^{-31}$ kg

$R = 8.314$ J/(K mol) $R = 0.08206$ L atm K^{-1} mol^{-1}

$R_H = 2.17987 \times 10^{-18}$ J

$e = 1.60218 \times 10^{-19}$ C   1 eV $= 1.60218 \times 10^{-19}$ J

$\varepsilon_0 = 8.8542 \times 10^{-12}$ C^{2}J^{-1}m^{-1}

$K_w = 1.00 \times 10^{-14}$ & 14.00 = pH + pOH at 25.0°C

$\Im$ (Faraday's constant) = 96,485 C mol^{-1}

Electromagnetic Spectrum:
Violet ~ 400-430 nm
Blue ~ 431-490 nm
Green ~ 491-560 nm
Yellow ~ 561-580 nm
Orange ~ 581-620 nm
Red ~ 621-700 nm

Complementary Colors: red/green, blue/orange, yellow/violet

$I^- < Br^- < Cl^-$ (weak field ligands)
$< F^- < OH^- < H_2O$ (intermediate)
$< NH_3 < CO < CN^-$ (strong field ligands)

1 C • V = 1 J   1 J = 1 kgm^{2}s^{-2}

1A = 1C/s   1W = 1 J/s

ln = 2.3025851log

1 Bq = 1 nuclei/sec

$x = [-b \pm (b^2 - 4ac)^{1/2}]/2a$ $ax^2 + bx + c = 0$

K.E. $= \frac{1}{2}mv^2$ $p = mv$ $\lambda = \dfrac{h}{p}$

$E = h\nu = hc/\lambda$ $c = \nu\lambda$

$E_n = -\dfrac{Z^2 R_H}{n^2}$ $E_{nl} = -\dfrac{Z_{eff}^2 R_H}{n^2}$

for $n_f < n_i$ ......   for $n_f > n_i$ .....

$v = \dfrac{Z^2 R_H}{h}\left(\dfrac{1}{n_f^2} - \dfrac{1}{n_i^2}\right)$ $v = \dfrac{Z^2 R_H}{h}\left(\dfrac{1}{n_i^2} - \dfrac{1}{n_f^2}\right)$

$U(r) = (z_1 z_2 e^2)/(4\pi\varepsilon_a r)$

Electronegativity = (IE + EA)/2

$\Delta H_r° = \Sigma\Delta H_B(\text{reactants}) - \Sigma\Delta H_B(\text{products})$
$\Delta H_r° = \Sigma\Delta H_f°(\text{products}) - \Sigma\Delta H_f°(\text{reactants})$
$\Delta S_r° = \Sigma S°(\text{products}) - \Sigma S°(\text{reactants})$
$\Delta G_r° = \Sigma\Delta G_f°(\text{products}) - \Sigma\Delta G_f°(\text{reactants})$

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

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

$\Delta G = RT \ln Q/K$

$\ln(K_2/K_1) = -(\Delta H°/R)(1/T_2 - 1/T_1)$

$PV = nRT$

$s = k_H P$

$pH \approx pK_a - \log([HA]/[A^-])$

$pH = -\log[H_3O^+]$ $pOH = -\log[OH^-]$

$K_w = K_a K_b$ $pK = -\log K$

$Q = It$

$\Delta G°_{cell} = -(n)(\Im)\,\Delta E°_{cell}$

$\Delta E°(\text{cell}) = E°(\text{cathode}) - E°(\text{anode})$

$\Delta E° = E°(\text{reduction}) - E°(\text{oxidation})$

$\Delta E_{cell} = E°_{cell} - (RT/n\Im)\ln Q$

$\Delta E_{cell} = E°_{cell} - [(0.025693 \text{ V})(\ln Q)/n]$ at 25.0°C

$\ln K = (n\Im/RT)\,\Delta E°$

$A = A_o e^{-kt}$ $N = N_o e^{-kt}$ $A = kN$

$[A] = [A]_o e^{-kt}$ $t_{1/2} = \ln2/k$

$1/[A] = 1/[A]_o + kt$ $t_{1/2} = 1/k[A]_o$

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

$\ln(k_2/k_1) = -(E_a/R)(1/T_2 - 1/T_1)$

$d[P]/dt = (k_2[E]_o[S])/([S] + K_m)$

$V_{max} = k_2[E]_o$

The Active Metals | **The Nonmetals** | **Noble Gases**

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18ᵃ VIIIAᵇ
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.29
55 Cs 132.905	56 Ba 137.33	57 La 138.905	*72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.966	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	89 Ac 227.028	†104 Unq (261)	105 Unp (262)	106 Unh (263)												

Transition Elements

Inner Transition Metals

* Lanthanides

58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	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)

† Actinides

5.111 Principles of Chemical Science
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