SCORING – DO NOT REMOVE THIS SHEET FROM THE FRONT OF THE EXAM

Section 1: 47 / 50

Section 2: 47 / 60

Section 3: 40 / 40

Section 4: 33 / 50

Section 5: 31 / 31

Section 6: 28 / 28

Total: 226 /259

great job!

PERIODIC TABLE OF THE ELEMENTS

http://www.ktf-split.hr/periodni/en/

GROUP NUMBERS IUPAC RECOMMENDATION (1985) — 13

GROUP NUMBERS CHEMICAL ABSTRACT SERVICE (1986) — IIIA

ATOMIC NUMBER — 5 | 10.811 — RELATIVE ATOMIC MASS (1)

SYMBOL — B

BORON — ELEMENT NAME

PERIOD	GROUP 1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 1.0079 H HYDROGEN																	2 4.0026 He HELIUM
2	3 6.941 Li LITHIUM	4 9.0122 Be BERYLLIUM											5 10.811 B BORON	6 12.011 C CARBON	7 14.007 N NITROGEN	8 15.999 O OXYGEN	9 18.998 F FLUORINE	10 20.180 Ne NEON
3	11 22.990 Na SODIUM	12 24.305 Mg MAGNESIUM											13 26.982 Al ALUMINIUM	14 28.086 Si SILICON	15 30.974 P PHOSPHORUS	16 32.065 S SULPHUR	17 35.453 Cl CHLORINE	18 39.948 Ar ARGON
4	19 39.098 K POTASSIUM	20 40.078 Ca CALCIUM	21 44.956 Sc SCANDIUM	22 47.867 Ti TITANIUM	23 50.942 V VANADIUM	24 51.996 Cr CHROMIUM	25 54.938 Mn MANGANESE	26 55.845 Fe IRON	27 58.933 Co COBALT	28 58.693 Ni NICKEL	29 63.546 Cu COPPER	30 65.39 Zn ZINC	31 69.723 Ga GALLIUM	32 72.64 Ge GERMANIUM	33 74.922 As ARSENIC	34 78.96 Se SELENIUM	35 79.904 Br BROMINE	36 83.80 Kr KRYPTON
5	37 85.468 Rb RUBIDIUM	38 87.62 Sr STRONTIUM	39 88.906 Y YTTRIUM	40 91.224 Zr ZIRCONIUM	41 92.906 Nb NIOBIUM	42 95.94 Mo MOLYBDENUM	43 (98) Tc TECHNETIUM	44 101.07 Ru RUTHENIUM	45 102.91 Rh RHODIUM	46 106.42 Pd PALLADIUM	47 107.87 Ag SILVER	48 112.41 Cd CADMIUM	49 114.82 In INDIUM	50 118.71 Sn TIN	51 121.76 Sb ANTIMONY	52 127.60 Te TELLURIUM	53 126.90 I IODINE	54 131.29 Xe XENON
6	55 132.91 Cs CAESIUM	56 137.33 Ba BARIUM	57-71 La-Lu Lanthanide	72 178.49 Hf HAFNIUM	73 180.95 Ta TANTALUM	74 183.84 W TUNGSTEN	75 186.21 Re RHENIUM	76 190.23 Os OSMIUM	77 192.22 Ir IRIDIUM	78 195.08 Pt PLATINUM	79 196.97 Au GOLD	80 200.59 Hg MERCURY	81 204.38 Tl THALLIUM	82 207.2 Pb LEAD	83 208.98 Bi BISMUTH	84 (209) Po POLONIUM	85 (210) At ASTATINE	86 (222) Rn RADON
7	87 (223) Fr FRANCIUM	88 (226) Ra RADIUM	89-103 Ac-Lr Actinide	104 (261) Rf RUTHERFORDIUM	105 (262) Db DUBNIUM	106 (266) Sg SEABORGIUM	107 (264) Bh BOHRIUM	108 (277) Hs HASSIUM	109 (268) Mt MEITNERIUM	110 (281) Uun UNUNNILIUM	111 (272) Uuu UNUNUNIUM	112 (285) Uub UNUNBIUM		114 (289) Uuq UNUNQUADIUM				

LANTHANIDE

6	57 138.91 La LANTHANUM	58 140.12 Ce CERIUM	59 140.91 Pr PRASEODYMIUM	60 144.24 Nd NEODYMIUM	61 (145) Pm PROMETHIUM	62 150.36 Sm SAMARIUM	63 151.96 Eu EUROPIUM	64 157.25 Gd GADOLINIUM	65 158.93 Tb TERBIUM	66 162.50 Dy DYSPROSIUM	67 164.93 Ho HOLMIUM	68 167.26 Er ERBIUM	69 168.93 Tm THULIUM	70 173.04 Yb YTTERBIUM	71 174.97 Lu LUTETIUM

ACTINIDE

7	89 (227) Ac ACTINIUM	90 232.04 Th THORIUM	91 231.04 Pa PROTACTINIUM	92 238.03 U URANIUM	93 (237) Np NEPTUNIUM	94 (244) Pu PLUTONIUM	95 (243) Am AMERICIUM	96 (247) Cm CURIUM	97 (247) Bk BERKELIUM	98 (251) Cf CALIFORNIUM	99 (252) Es EINSTEINIUM	100 (257) Fm FERMIUM	101 (258) Md MENDELEVIUM	102 (259) No NOBELIUM	103 (262) Lr LAWRENCIUM

(1) Pure Appl. Chem., 73, No. 4, 667-683 (2001)
Relative atomic mass is shown with five significant figures. For elements have no stable nuclides, the value enclosed in brackets indicates the mass number of the longest-lived isotope of the element.
However three such elements (Th, Pa, and U) do have a characteristic terrestrial isotopic composition, and for these an atomic weight is tabulated.

Editor: Aditya Vardhan (adivar@netllinx.com)

Values of Some Physical Constants

Constant	Symbol	Value
Atomic mass constant	*amu*	$1.660\ 5402 \times 10^{-27}$ kg
Avogadro constant	N_A	$6.022\ 1367 \times 10^{23}$ mol^{-1}
Bohr magneton	$\mu B = e\hbar/2m_e$	$9.274\ 0154 \times 10^{-24}$ J · T^{-1}
Bohr radius	$a_0 = 4\pi\varepsilon_0^2/r_e e^2$	$5.291\ 772\ 49 \times 10^{-11}$ m
Boltzmann constant	k_B	$1.380\ 658 \times 10^{-23}$ J · K^{-1}
		0.695 038 cm^{-1}
Electron rest mass	m_e	$9.109\ 3897 \times 10^{-31}$ kg
Gravitational constant	G	$6.672\ 59 \times 10^{-11}$ · m^3 · kg^{-1} · s^{-2}
Molar gas constant	R	8.3145101 J · K^{-1} · mol^{-1}
		0.083 1451 dm^3 · bar K^{-1} · mol^{-1}
		0.082 0578 dm^3 · atm K^{-1} · mol^{-1}
Molar volume, ideal gas		
(one bar, 0°C)		22.711 08L · mol^{-1}
(one atm, 0°C)		22.414 09 L · mol^{-1}
Nuclear magneton	$\mu_N = e\hbar/2m_p$	$5.050\ 7866 \times 10^{-27}$ J · T^{-1}
Permittivity of vacuum	ε_0	$8.854\ 187\ 816 \times 10^{-12}$ C^2 · J^{-1} · m^{-1}
	$4\pi\varepsilon_0$	$1.112\ 650\ 056 \times 10^{-10}$ C^2 · J^{-1} · m^{-1}
Planck constant	h	$6.626\ 0755 \times 10^{-34}$ J · s
	$\hbar$	$1.054\ 572\ 66 \times 10^{-34}$ J · s
Proton charge	e	$1.602\ 177\ 33 \times 10^{-19}$ C
Proton magnetogyric ratio	γ_p	$2.675\ 221\ 28 \times 10^{8}$ s^{-1} · T^{-1}
Proton rest mass	m_p	$1.672\ 6231 \times 10^{-27}$kg
Rydberg constant (Bohr)	$R_\infty = m_e e^4/8\varepsilon_0^2 h^2$	$2.179\ 8736 \times 10^{-23}$ J
		109 737.31534 cm^{-1}
Rydberg constant for H	R_H	109677.581 cm^{-1}
Speed of light in vacuum	c	299 792 458 m · s^{-1} (defined)
Stefan-Boltzmann constant	$\sigma = 2\pi^5 k_B^4/15h^3c^2$	$5.670\ 51 \times 10^{-8}$ J · m^{-2} : K^{-4} · s^{-1}

Section 1. (50 pts) Glowstick Kinetics (you will have up to 25 minutes to work on the lab portion but you may perform calculations and work later)

Materials

3 glow sticks (4" long, ~10 mm diameter)
~12x12" piece of Al foil
tongs
thermometer
3 beakers
ice
hot water bath (set to ~40°C)
Labquest Spectrometer

<u>Goal</u>: Using the above equipment, determine the activation energy E_a for the lightstick reaction.

A simplified version of the glowstick reaction is:

$A + B \rightarrow C$

$C + D \rightarrow D^*$

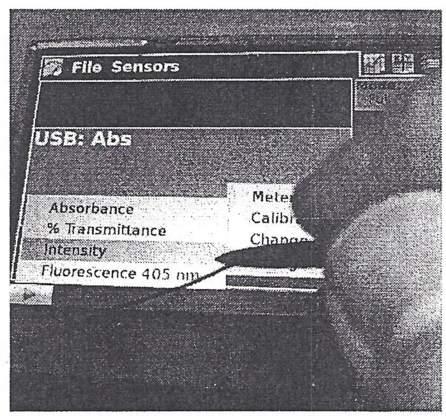
$D^* \rightarrow D + h\upsilon$

Since photons ($h\upsilon$) are a "product" one can measure reaction *rate* directly by measuring the intensity (photons/time/area) coming from the lightstick.

Instructions /tips:

0) Read the whole problem even if you can't do all parts

1) You **MUST** set your Labquest pro to ***intensity mode***. To do this tap on the USB: ____ screen, then select Intensity (see photo at right, if there is a problem, ask your TA for help)



2) You can measure the intensity vs. wavelength spectrum of the glow stick by placing it into the cuvette holder after pressing the "play" button

3) What wavelength do you want to measure the light at?

4) do you need to (manually) subtract a background?

600

5) make sure you shake your glowstick so that there are no bubbles at the bottom where you are measuring the light from

6) Start your lightsticks ALL at the same time. Let them run for 5-10 minutes before using them. Cycle through them. They have a fast initial decay so if you wait a long time between measuring one stick and another the difference will be complicated by their decay in time.

7) Do NOT turn the hot plates up past 40 C. The higher temperatures will damage your light sticks.

K7

Section 1. Glow sticks Data table (for convenience only)

T(C)	Intensity	1/T (K)	ln(intensity)				
40C	0.215 rel	0.00319	-1.537				
34.5	0.139 rel	0.00325	-1.973				
31.6	0.129	0.00328	-2.048				
0	0.095	0.003366	-2.354				
25.1	0.117	0.00335	-2.15				

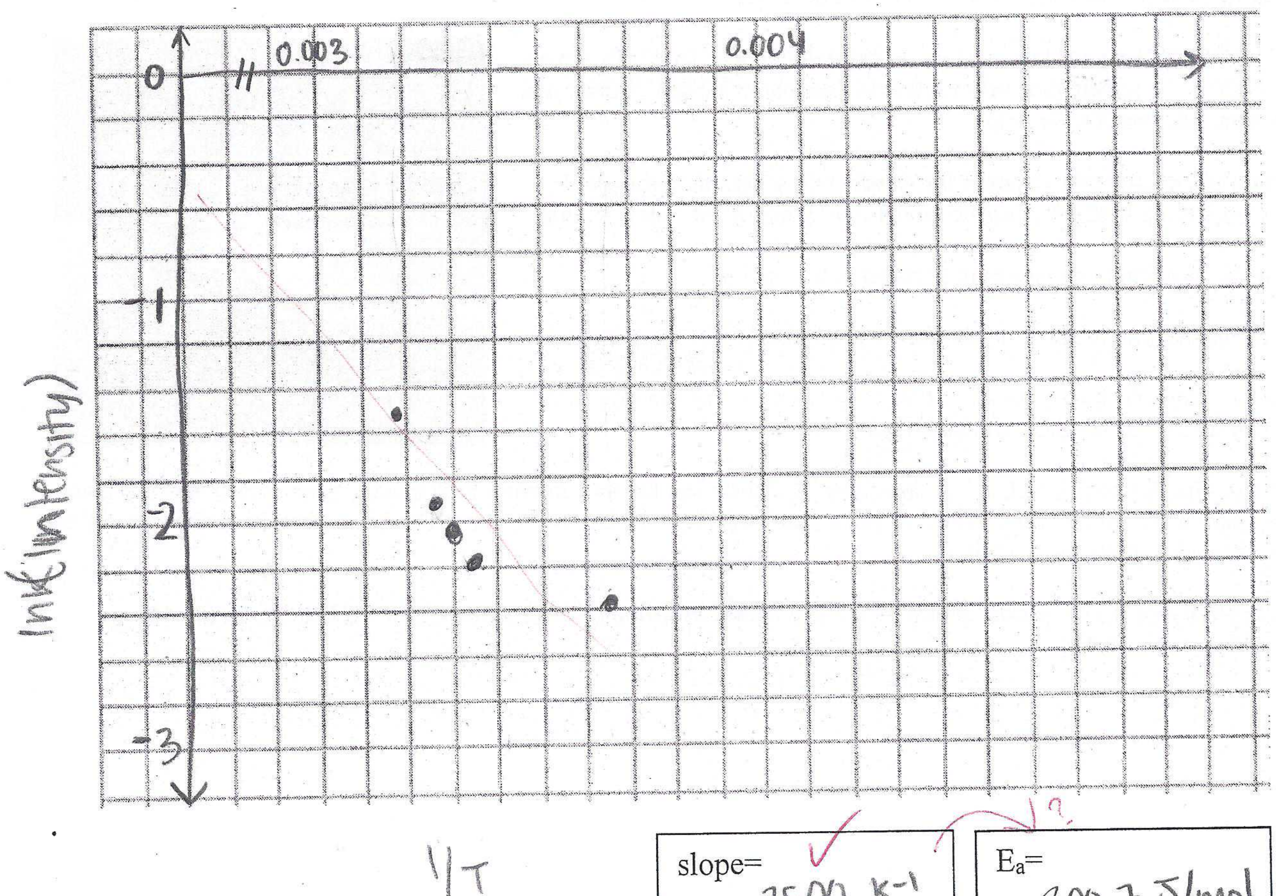
(A) (5 pts) Write down the Arrhenius equation relating activation energy, temperature and reaction rate:

x5 $K = Ae^{-Ea/RT}$ ∴ $\ln K = \ln A - \frac{Ea}{R}\left(\frac{1}{T}\right)$

(B) (25 pts) Plot your data below in order to determine Ea in kJ/mol (R = 8.314 J mol^{-1} K^{-1}). Label your axes. Show your work.

x10

Describe what you are plotting 1/T vs. ln(intensity) **(5 pts)**



slope= ✓ $-2500\ K^{-1}$

?

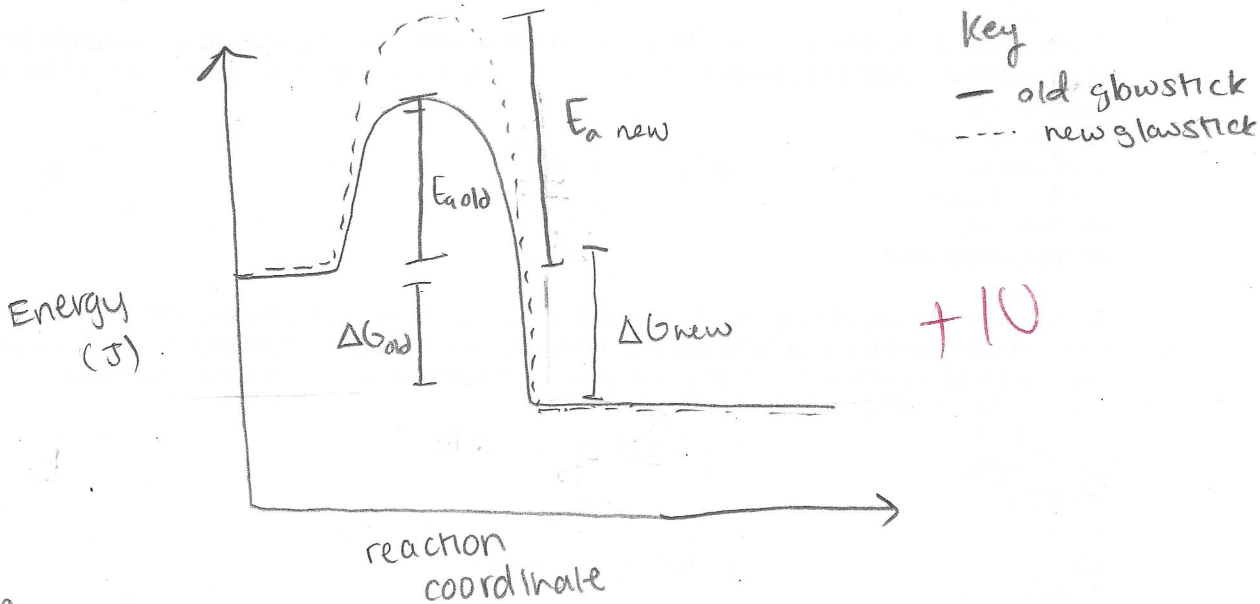
E_a= 300.7 J/mol

$-\left(\frac{-2500\ K^{-1}}{8.314\ J/molK}\right) =$

$m = \frac{\Delta y}{\Delta x} = \frac{-2.048 + 1.973}{0.00328 - 0.00325\ K^{-1}} = -2500$

27

1C) (10 Points) A new glowstick reaction is found that is more sensitive to variations in light emission with temperature. Sketch 2 plots of energy vs. reaction coordinate for these two reactions one labeled "New glow stick" and one labeled "old glowstick", label ΔG and E_a on both plots.



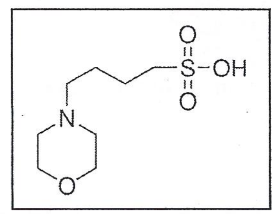
+10

$K = Ae^{-E_a/RT}$

more sensitive to var in temp = higher E_a

E_a new > E_a old

1D) (10 points) The structure of MOBS is shown at right. Calculate the pH of a 0.1M MOBS solution in water, given the MOBS pKa = 7.6. Yeah redemption points! oh no.

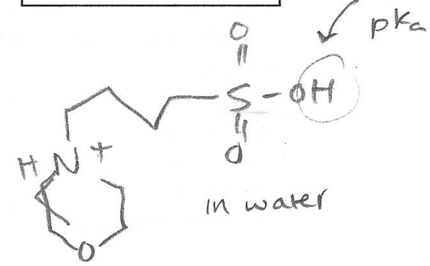


MOBS	⇌	$MOBS^-$	+ H^+
0.1M		0	0
		x	x
		x	+x

$$\frac{x^2}{0.1-x} = 10^{-7.6}$$

$x = 5.01e{-5}M$

+10



$-\log(5.01e{-5}M) = \boxed{4.3}$

that seems slightly too acidic?
even if $pKa_1 = 2.2$ ish or whatever

20

Section 2. (60 pts) Multiple Choice – WRITE YOUR ANSWER IN THE BOX
(-1 point for an incorrect guess on any problem) (4 points each)
More GRE-like and MCAT-like questions to help you practice

rate = $\frac{V[S]}{K_m+[S]}$

1) Many enzyme reactions follow the rate law shown above, where V and K_m are constants and $[S]$ is the concentration of substrate that is undergoing a catalyzed reaction. When $[S] \gg K_m$, what is the apparent order of the reaction?
(A) Zero order
(B) One-half order
(C) First order
(D) Second order
(E) Third order
(F) None of the above

$$\text{rate} = \frac{V\cancel{[S]}}{\cancel{[S]}} = V$$

1) A

2) ^{123}I is decays via electron capture with a half-life of 13.22h followed by emission of 159 keV and 27 keV gamma rays. ^{123}I is used in nuclear medicine imaging supplied as sodium iodide. The packaging reads that at calibration time, each capsule has an activity of 3.7 MBq, (100 μCi). Each gelatin capsule contains not more than 1 g of sucrose. What mass of ^{123}I is in a single capsule at calibration time?
(A) 97,000 fg
(B) 52,000 fg
(C) 5.2 pg
(D) 9.7 mg
(E) 9.7 μg
(F) none of the above

$3.7E6\,Bq = kN$

$\frac{3.7E6\,Bq}{\ln 2/13.22 \cdot 3600} = N = 2.54E11$

$2.54E11 \cdot \frac{1\,mol}{6.02E23} \cdot \frac{123\,g}{1\,mol} = 5.19E{-11}\,g \cdot \frac{10^{12}}{1\,g}$

52pg

2) B

3) In a 0.1M solution of a weak acid, $[A^-] = [HA]$ at $[H^+]=3.47\times10^{-5}$, the pKa of this acid is closest to:
(A) 1.5
(B) 2.5
(C) 3.5
(D) 4.5
(E) 5.5
(F) none of the above

$$K_a = \frac{[H^+]\cancel{[A^-]}}{\cancel{[HA]}} = 3.47E{-5}$$

3) D

4) A star with a surface temperature of 6000K emits photons of many energies. What is the energy of red photons with $\lambda = 620$ nm, being emitted by the star (in eV)?
(A) 3.0
(B) 2.0
(C) 1.0
(D) 3.2×10^{-19}
(E) 9.9×10^{-17}
(F) none of the above

$E = h\cancel{c}/\lambda$

$$\frac{1240\,eV\,nm \quad \cancel{6.626E{-34} \times 3E8}}{620\,nm \cdot \cancel{\frac{1m}{10^9 nm}}} = 2$$

4) B

5) ^{11}C decays by positron emission to form ^{11}B. If the mass of an ^{11}B atom is 11.0093055 amu and the mass of an ^{11}C atom is 11.011433 amu and the electron mass is 0.00054858 amu, and 1 amu = 931.5 MeV/c^2, then maximum KE of the positron emitted is closest to:
(A) 0.449 MeV
(B) 0.960 MeV
(C) 1.47 MeV
(D) 1.98 MeV
(E) none of the above

$^{11}C \rightarrow {}^{0}_{+1}e^+ + {}^{11}_{5}B + \nu_e$

$$E = \Delta mc^2 = \left(\begin{matrix}(11.0093055) \\ +2(0.00054858) \\ -11.011433\end{matrix}\right)\cancel{c^2} \cdot 931.5\,MeV/\cancel{c^2} =$$

$-0.00103 \cdot 931.5$

5) B

6) An electron is
(A) made from quarks
(B) made from neutrinos
(C) a meson
(D) a baryon
(E) a lepton
(F) a leprechaun yes can't see it
(G) none of the above

6) E

7) A radioactive isotope of Copper, ^{64}Cu, decays via beta emission to form ^{64}Zn with a half-life of 12.8 hours. Starting with 200g of ^{64}Cu, how much ^{64}Zn is produced in 25.6 hours?
(A) 200.0 g
(B) 150.0 g
(C) 138.6 g
(D) 100.0 g
(E) 40.0 g
(F) 25.0 g
(G) none of the above

7) B

2 half lives

$\frac{200}{2} = 100 + \frac{100}{2} = 150$

8) ^{99m}Tc is a radioisotope used in nuclear medicine. It decays to ^{99}Tc by emission of 140 keV gamma rays with a half life of 6.0 hours. If the initial activity of a sample is 200 MBq, what is the momentum of a photon being emitted 12 hours later?
(A) $2.24\text{x}10^{-14}$ J
(B) $2.24\text{x}10^{-14}$ kg m/s
(C) $7.46\text{x}10^{-23}$ kg m/s
(D) $8.85\text{x}10^{-3}$ kg m/s
(E) 50 MBq
(F) 35 keV
(G) None of the above

8) C

$E = pc$

$\frac{E}{c} = p = \frac{140\,\text{BeV}}{3\text{E}8\,\text{m/s}} \cdot \frac{1.602\text{E-}19\,\text{J}}{1\text{eV}} =$

2014

9) Given the following mechanism in which neither step can be considered rate limiting:

$A + M \leftrightarrow A^* + M$ (rates: k_1 forward, k_{-1} reverse)
$A^* \rightarrow P$ (rate: k_2 forward)

The rate expression is best given by:
(A) $d[P]/dt = -k_1k_2[A][M]/k_{-1}[M]$
(B) $d[P]/dt = k_1[A][M]/(k_{-1}[M]+ k_1)$
(C) $d[P]/dt = k_1k_2[A][M]/(k_{-1}[M] + k_2)$
(D) $d[P]/dt = k_1[A][M]$
(E) $d[P]/dt = k_1k_2[A]/[M]$
(F) none of the above

9) C

$[A^*] = [A][M]k_1 - k_{-1}[A^*][M] - [A^*]k_2$

$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2}$

$\frac{d[P]}{dt} =$

10) An electron has an uncertainty in its position of 1Å. What is the minimum uncertainty the momentum of this electron?
(A) $6.63\text{x}10^{-24}$
(B) $3.31\text{x}10^{-24}$ J
(C) $5.3\text{x}10^{-25}$ J uh
(D) $5.3\text{x}10^{-25}$
(E) None of the above

h is in units of momentum

m ΔP

$\frac{kgm^2/s^2}{m}$ = Js

kgm/s²

Js/m = kgm²/s²

$\Delta x \Delta p \geq h/4\pi$

$\Delta p \geq \frac{6.626\,\text{Js} \cdot 10^{-34}}{4\pi\,(1\text{Å} \cdot \frac{1\text{m}}{10^{10}\text{Å}})} \geq$ 5.27E-25 kgm/s²

10)

11) The function $f(x,t) = sin(kx)cos(\omega t)$ is an example of a:
(A) function I never want to see again yes
(B) wave travelling in the +x direction (to the right)
(C) classical 1D standing wave
(D) quantum mechanical 1D standing wave
(E) wave travelling in the –x direction (to the left)

11) C ✓

12) The Bohr model explains the Rydberg equation, and predicts the UV-visible emission spectrum of the hydrogen atom. A form of the Bohr model / Rydberg equation may also be used to predict the UV-visible emission for all of the following EXCEPT:
(A) helium cation, He^{+} ✓
(B) deuterium atom, D $^{2}_{1}H^{+}$
(C) beryllium cation, Be^{3+} ✓
(D) hydride ion, H^{-} ✓?
(E) tritium atom what is this
(F) All of the above can be predicted

single electron

12)

13) If z = 3+ 5i, then z^{*} z =
(A) 8
(B) -16
(C) +16
(D) 34
(E) 3
(F) none of the above

$(3+5i)(3-5i)$

$9+(25)i^2 = -16$

but always positive!

13) C ✗

14) An electron is confined to a 1D box with infinitely high walls. If the box was 1 nm wide, the electron could absorb photons of energy:
(A) 0.377 eV
(B) 1.13 eV
(C) 1.13×10^{-9} eV
(D) 1.77 eV
(E) None of the above

$E_n = \frac{n^2 h^2}{8 m L^2} = 6.02E\text{-}20\,J$

$= 0.377\,eV$

14) A ✓

15) If a wavefunction $\psi(x)$ is normalized, then it means that:
(A) $\psi^*(x)\ \psi(x) = 1$
(B) $\psi^*(x)\ \psi(x) = 0$
(C) $\int_{-\infty}^{\infty} \psi^*(x)\ \psi(x) dx = 0$
(D) $\int_{-\infty}^{\infty} \psi^2(x)\ dx = 1$
(E) $\int_{-\infty}^{\infty} \psi^*(x)\ \psi(x) dx = 1$
(F) none of the above

15) E ✓

12(4) − 1 = 47

Section 3. (40 pts) Catalysis, Enzymes, and the Steady State Approximation
3. Kinetics
The classic mechanism for an enzyme catalyzed reaction is:

$$E + S \underset{k_{-1}}{\overset{k_1}{\leftrightarrow}} ES$$

$$ES \xrightarrow{k_2} E + P$$

Where E is the free enzyme, S is the substrate, and P is the product.

(3.A.1) (5 pts) State the key assumption of the steady state approximation:

$$\frac{d[ES]}{dt} = 0 \quad , \quad \text{no rate-limiting step}$$

5

(3.A.2) (10 pts) Apply the steady state approximation to this mechanism to derive the expression for the rate of product formation, d[P]/dt in terms of substrate concentration [S], total enzyme concentration [E_T], and the Michaelis-Menten constant, $K_m = (k_{-1} + k_2) / k_1$ Show all work. Circle your key steps (especially what d[ES]/dt = ?,)

$$\frac{d[ES]}{dt} = K_1[E][S] - K_{-1}[ES] - K_2[ES] = 0$$

$$[E_T] = [E] + [ES] \therefore [E_T] - [ES] = [E]$$

10

$$\frac{d[ES]}{dt} = 0 = K_1[E_T][S] - K_1[ES][S] - K_{-1}[ES] - K_2[ES]$$

$$[ES] = \frac{K_1[E_T][S]}{K_1[S] + K_{-1} + K_2}$$

$$\frac{d[P]}{dt} = K_2[ES] = \frac{K_1K_2[E_T][S]}{K_1[S] + K_{-1} + K_2}\left(\frac{1/K_1}{1/K_1}\right)$$

note: $\frac{K_{-1}+K_2}{K_1} = K_m$ here!

$$\boxed{\frac{d[P]}{dt} = \frac{K_2[E_T][S]}{K_m + [S]}}$$

15

(3.B) (15 pts) Glucose oxidase is an enzyme that catalyzes the oxidation of beta-D-glucose to hydrogen peroxide and D-glucono-δ-lactone. It is widely used in diagnostic assays, such as tests for blood sugar levels. It has an approximate K_m = 50 mM, and $k_{cat} = k_2 = 1000\ s^{-1}$. *On the graph below, sketch d[P]/dt vs. [S], for the entire interesting range of behavior if the total concentration of glucose oxidase is $1x10^{-6}$ molar.* Label V_{max} and K_m and make sure they fall at the correct values.

$K_2[E_T] = V_{max}$

$1000\,s^{-1} \cdot 1E\text{-}6M = 0.001M/s$

(3C) (5 pts) Under what conditions will the oxidation of glucose substrate by the glucose oxidase enzyme appear to be *zeroth* order in [glucose]? (use equations for full credit)

$\frac{d[P]}{dt} = \frac{K_2[S][E_T]}{[S]+K_m}$

looks zeroth order in [glucose] when [glucose] >> Km or [glucose] >> 50mM because

when [S] >> Km

$\frac{d[P]}{dt} = \frac{K_2\cancel{[S]}[E_T]}{\cancel{[S]} + 0_{ish}}$

then $\frac{d[P]}{dT} = K_2[E_T] = 0.001\,M/s$

5

(3D) (5 pts) Under what conditions will the oxidation of glucose substrate by the glucose oxidase enzyme appear to be *first* order in [glucose]? (use equations for full credit)

first order in glucose when Km >> [glucose] or 50mM >> [glucose]

$\frac{d[P]}{dt} = \frac{K_2}{K_m}[S][E_T]$ then or $\frac{d[P]}{dt} = (0.02\,s^{-1}M^{-1})[glucose]$

5

because $\frac{d[P]}{dt} = \frac{K_2[S][E_T]}{K_m + \cancel{[S]}^{\to 0 \text{ basically}}}$

25

Section 4. (50 points) Nuclear

Approved in 2013, $^{223}RaCl_2$ (FW=296.81 g/mol) became the first alpha emitter ever to be licensed for use as a radiopharmaceutical in the United States and is now marketed under the trade name Xofigo. As a calcium mimetic, $^{223}Ra^{2+}$ is taken up preferentially in regions of osteoblastic metastasis (bone tumors) and has been shown to improve survival rates and quality of life for castration resistant prostate cancer patients with symptomatic bone metastases. ^{223}Ra decays via alpha emission with a half-life of **11.4 days.**

(A) (5 pts) In 1-2 sentences, explain why an alpha emitter such as ^{223}Ra might be preferable to a beta or gamma emitter for radiation therapy if the drug can be delivered specifically to the site of the cancer.

Alpha particles will travel less far into the tissue than beta or gamma rays and cause less tissue damage. It is heavier and less able to travel though tissue.

X

(B) (10 pts) The recommended dose of $^{223}RaCl_2$ is 50 kBq/kg (1 Bq = 1 decay / s), and is supplied as standardized solutions buffered for intravenous injection with 1000 kBq/ml activity at calibration time. What volume of solution (in mL) should you inject into a patient weighing 60 kg if it is now 2.0 days after the calibration date of your $^{223}RaCl_2$ solution?

volume= $\boxed{0.00339 \text{ mL}}$

$A = 1000e3 \frac{Bq}{mL} \cdot e^{-\ln 2/11.4 \cdot 2} = 885498 \text{ Bq/mL}$

$A = A_0 e^{-kt}$

$\frac{1 \text{ mL}}{885498 \text{ kBq}} \cdot \frac{50 \text{ kBq}}{kg} \cdot 60 \text{ kg} = 0.003387 \text{ mL}$

$1000 e^{-(\ln 2)/11.4 \cdot 2} = A_f$

+10

A_f ~~$\frac{500 \, Bq}{kg}$~~ ~~$\frac{A_f}{50 \, Bq}$~~ $\frac{1 L}{A_f} \cdot \frac{50 \, kg}{kg} \cdot 60 \, kg = mL$

X **(C) (10 points)** The biological half-life represents the time it takes the body to clear a compound metabolically. If the *biological* half-life for Ra^{2+} is 3.5 days, and the radioactive half-life is 11.4 days, calculate the activity of ^{223}Ra remaining in the 60 kg patient dosed with 50 kBq/kg 5 days after treatment.

activity= $\boxed{822.3 \text{ kBq}}$

$K_{bio} = 0.198 \text{ days}^{-1}$

$K_{rad} = 0.0608 \text{ days}^{-1}$

$K_{Total} = 0.259 \text{ days}^{-1}$

+10

$\frac{50 \text{ kBq}}{kg} \cdot 60 \text{ kg} \cdot \frac{1000 \text{ Bq}}{1 \text{ kBq}} \cdot e^{-0.259 \cdot 5} = A = 822332.9 \text{ Bq}$

$= 822 \text{ kBq}$

$\frac{50 \text{ kBq}}{kg} \cdot 60 \text{ kg} \cdot \frac{1000 \text{ Bq}}{1 \text{ kBq}} = A_0$

$A_0 = KN$ 0.198

$N = 15151515$

$15151515 e^{-0.259 \cdot 5} = N_f = 4149967$

$A = 4149967 \cdot 0.198$

$A = 822 \text{ kBq}$ idk same answer

activity should only take Krad into account? idk

25

(D) ^{223}Ra is produced by neutron bombardment of ^{226}Ra to produce ^{227}Ra. The ^{227}Ra then decays to ^{227}Ac with a half-life of **47 min**. ^{227}Ac decays to ^{227}Th with a half-life of **21.8 years**, and the resulting ^{227}Th in turn decays with a half-life of **18.7 days** to form ^{223}Ra which decays via alpha emission with a half-life of **11.4** days.

(5 pts) Write a balanced reaction for the decay of ^{227}Ra to ^{227}Ac:

$$^{227}_{88}Ra \rightarrow ^{227}_{89}Ac + ^{0}_{-1}e^- + \bar{\nu}_e$$

+5

(E) (20 pts) If 20 ng of freshly isolated ^{227}**Ra** is placed in solution, what will the mass of ^{223}**Ra** in that solution be after 100 days.

mass ^{223}Ra= $3.80 \cdot 10^{-14} g$

$$20ng \cdot \frac{1g}{10^9 ng} \cdot \frac{1mol}{227g} \cdot \frac{6.02e23}{1mol} = 5.304e12 = N$$

$$N_f = N_o e^{-kt}$$

$$K = \frac{\ln 2}{47min} \cdot \frac{60min}{1hour} \cdot \frac{24hours}{1day} = 21.24 \text{ days}^{-1}$$

$$N = (5.304e12)\, e^{-21.24 \cdot 100} = 0 \quad ^{227}Ra$$

✓ +3

$$N\ Ac = N_o\ ^{227}Ra$$

$$K_{Ac} = \frac{\ln 2}{21.8 \text{ years}} \cdot \frac{1 year}{365 \text{ days}} = 8.711e\text{-}5 \text{ days}^{-1}$$

$$N_f\ Ac = 5.304e12\, e^{-8.711e-5 \cdot 100} = 5.258e12$$

$$\therefore N_o\ ^{227}Th = 5.304e12 - 5.258e12 = 4.600e10$$

X

$$K_{227\,Th} = \frac{\ln 2}{18.7 days} = 0.037 \text{ days}^{-1}$$

$$N_{f\,Th} = 4.6e10 e^{-0.037 \cdot 100} = 1129797040$$

$$\therefore N_o\ ^{223}Ra = 4.487E10$$

$$K_{Ra} = \frac{\ln 2}{11.4} = 0.0608 \text{ days}^{-1}$$

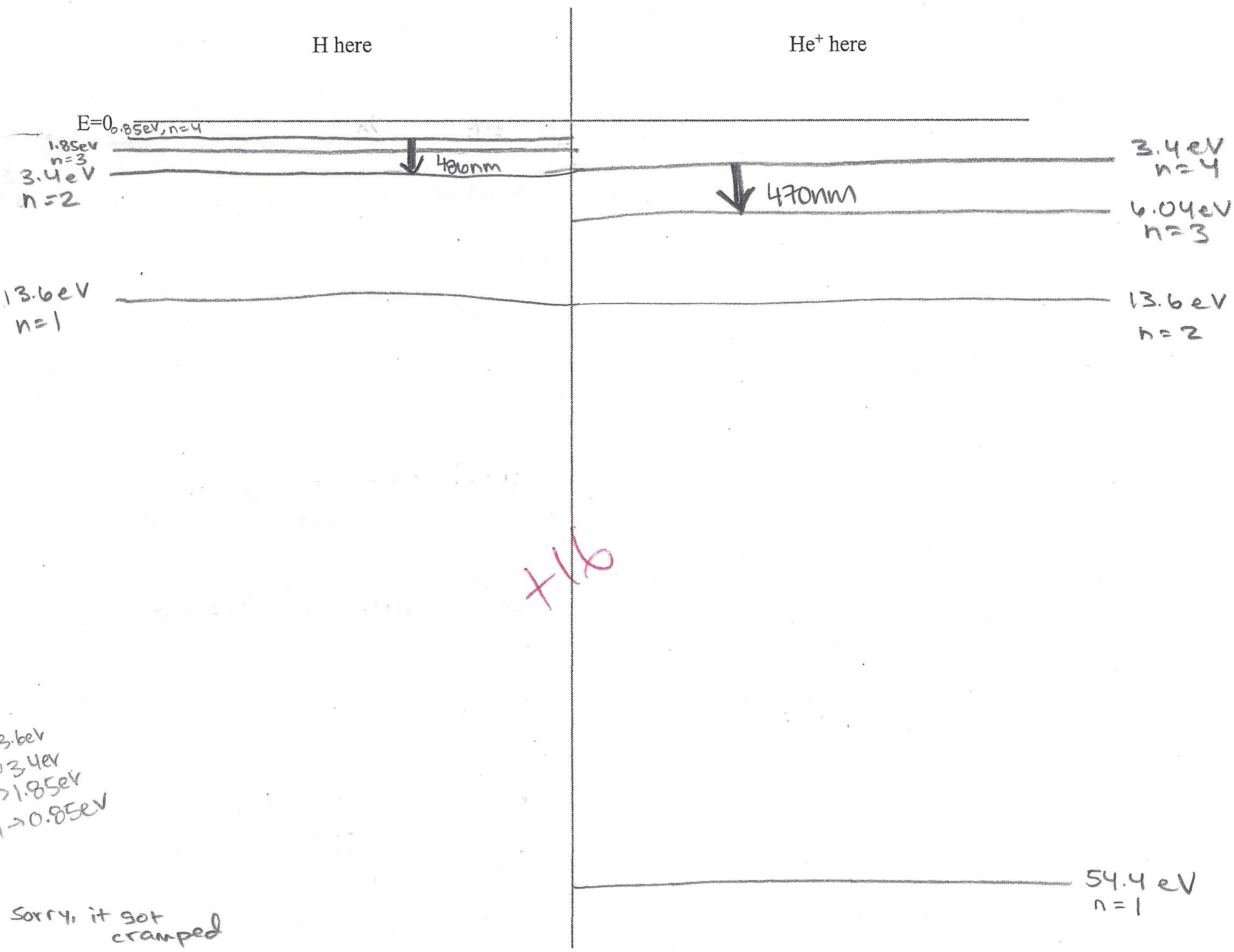
$$N_f\ ^{223}Ra = 4.487e10\, e^{-0.0608 \cdot 100} = 102653421.4$$

$$N_f\ ^{223}Ra \cdot \frac{1mol}{6.02e23} \cdot \frac{223g}{1mol} = 3.80E\text{-}14\ g = 38.02\ fg$$

8

Section 5 (31 pts) Bohr Model

(A) (16 points) Side by side (and crudely to scale) sketch the lowest ***four*** energy levels of an H-atom and He^{+} ion. Label each level with the quantum number "n" and the energy of the level. Keep the E=0 level constant for both.



n=1 → 13.6eV
n=2 → 3.4eV
n=3 → 1.85eV
n=4 → 0.85eV

Sorry, it got cramped

(B) (5 points) Comment on similarities / differences. Explain the physical origin of the difference in ground state energy using a formula OTHER than the Bohr model formula (I know you have the potential to answer this correctly!)

Both have energy levels at 13.6eV and 3.4eV. He^{+} has energy levels far higher than H does. He^{+} has a far higher ground state energy than He^{+} because it has more protons in the nucleus and stronger nuclear force.

Coulomb potential $= \left(9e9 \frac{Jm}{C^2}\right) \cdot \frac{q_1 q_2}{r}$ → lower potential for larger radius

Helium has higher potential energy that needs to be overcome to ionize?

+5

(C) (10 pts) When excited with a high voltage electrical discharge, H and He gas both emit many sharp lines. The H spectrum contains a line at 486 nm, and the He spectrum contains a line at 470 nm. Explain both by labeling your sketch above.

H → $\frac{hc}{\lambda} = E = \frac{1240 eV nm}{486 nm} = 2.551 eV$ → change from n=4 to n=2 (0.85eV − 3.4eV = 2.55eV)

He → $E = \frac{1240 eV nm}{470 nm} = 2.63 eV$ → change from n=4 to n=3 ((3.4eV − 6.04eV) = 2.64 eV)

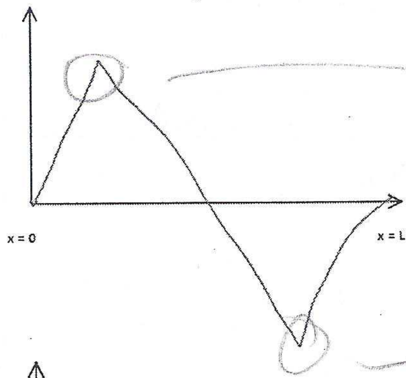
+10

31

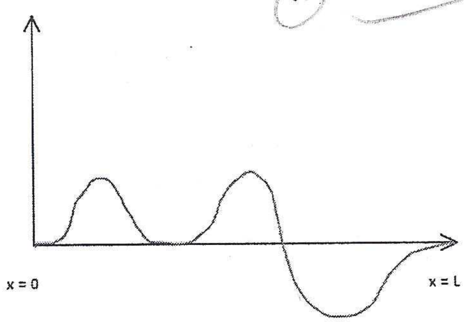
Section 6. (28 pts) Particle in a Box:

(A) (8 points) Indicate for each graph whether the function drawn could be a valid wave-function for a particle in a box with walls at x=0 and x=L Explain BRIEFLY. (4 points each)

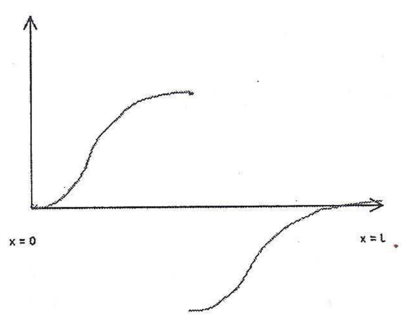
Graph | Valid / Reason



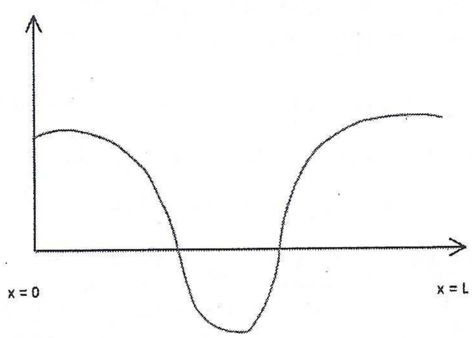
no $\psi^*\psi$ not ~~continous~~ continuous due to sharp changes in graph



yes, can be normalized
is continuous
0 @ x=0, x=L



no, not continuous



no, is not at 0 @ x=0, x=L

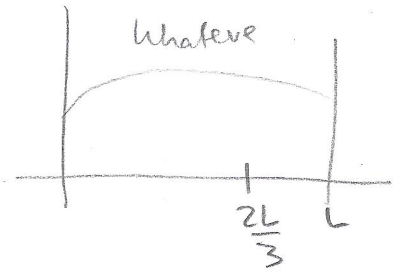
8

Section 6 – Particle in a Box

(B) (20 pts) The steady-state wave functions $\Psi_n(x)$ and the energy for a particle in the nth energy state in an infinite square box with walls at x = 0 and x = L are given by: $\Psi_n(x) = \sqrt{\frac{2}{L}}\sin\left(\frac{n\pi x}{L}\right), E_n = \frac{n^2 h^2}{8\,m\,L^2}$,
By explicit computation, determine the probability that the particle is found in the right-most 1/3 of the box for the 2nd excited state (n=3).

$\boxed{0.333}$

$$(\Psi_n(x))^2 = \frac{2}{L}\sin^2\left(\frac{3\pi x}{L}\right)$$



$$\frac{2}{L}\int_{\frac{2L}{3}}^{L} \sin^2\left(\frac{3\pi x}{L}\right) dx$$

$$= \frac{2}{2L}\int_{\frac{2L}{3}}^{L}\left(1-\cos\left(\frac{6\pi x}{L}\right)\right)dx \leftarrow \sin^2 u = \frac{1-\cos 2u}{2}$$

$$= \frac{1}{L}\left(x - \frac{L}{6\pi}\sin\frac{6\pi x}{L}\right)\Big]_{\frac{2L}{3}}^{L}$$

$$= \frac{1}{L}\left(L - \cancel{\frac{L}{6\pi}\sin 6\pi}^{\,0} - \left(\frac{2L}{3} - \cancel{\frac{L}{6\pi}\sin 4\pi}^{\,0}\right)\right)$$

$$= \frac{1}{L}\left(L-\frac{2L}{3}\right) = \left(1-\frac{2}{3}\right) = \frac{1}{3} = 0.333$$

wtf.

check according to calculator $2\int_{2/3}^{1}\left((\sin(3\pi x))^2\right)dx = 0.333$

20

4:30

KINETICS

Integrated Rate Laws:
1st: $\ln[A] = \ln[A_0] - kt$

2: $\frac{1}{[A]} = \frac{1}{[A_0]} + 2kt$

0: $[A] = [A]_0 - kt$

Arrhenius
$k = Ae^{-E_a/RT}$

$\ln k = \ln A - E_a/RT$

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

react coord.: geo. parameter for pos. of atoms

Michaelis-Menton:
$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES$ E = free enzyme

$ES \xrightarrow{k_2} E + P$

$\frac{d[ES]}{dt} = 0 =$ steady state approx

$K_m = \frac{k_{-1} + k_2}{k_1}$

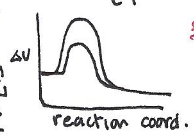
$[ES] = \frac{[E_T][S]k_2}{K_m + [S]}$

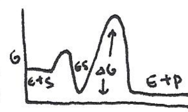
$k_{cat} \equiv \frac{V_{max}}{E_T}$

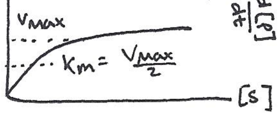
$\frac{dP}{dt} = k_2[E_T][S]$ when $[S] \ll K_m$; $[S] \gg K_m$, $k_2[E_T] = \frac{d[P]}{dt}$

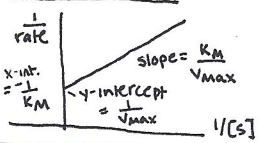
$\frac{d[P]}{dt} = \frac{k_2[E_T]}{1 + \frac{K_m}{[S]}}$

$[E_T] = [E] + [ES]$









CONSTANTS/EQ

Physics
$F = ma$ $KE = \frac{1}{2}mv^2$

$p = mv$

Gas $KE = \frac{3}{2}k_bT$

Normal units

$1N = kg\,m^2/s^2$

$J = Nm$

e^- charge $= 1.6e\text{-}19C$

$V = J/C$ $A = C/s$

$W = J/s$

$F = 96485\ C/mol$

$eV = 1.602e\text{-}19J$

$Bq = s^{-1} = Hz$

$Gy = J/kg = 100\ rad = $ dose

$Sv = 100\ rem$

$LD_{50} = 5\ Sv$

$\text{bkgd rad} = 2\ mSv$

Radioactivity
$m_p = 1.6726e\text{-}27kg = 938\ MeV/c^2$

$m_n = 1.6749e\text{-}27kg = 939.5\ MeV/c^2$

$m_e = 9.109e\text{-}31kg = 0.511\ MeV/c^2$

$1u = 931.494\ MeV$

Quantum Mech
$hc = 1240\ eV\,nm$

$h = 6.626e\text{-}34\ Js$

$1\ rydberg = 2.18e\text{-}18J$

$\hbar = h/2\pi$

$a_0 = 0.529 Å$

$\epsilon_0 = 8.854e\text{-}12\ C^2$

$\exp(x) \approx 1 + x$

Conversions
Mega = 1e6

milli = 10^-3

micro = 10^-6

nano = 10^-9

pico = 10^-12

1Å = 10^-10

Tera = 10^12

giga = 10^9

kilo = 10^3

femto = 10^-15

most reactive: K, Na, Ca, Mg, Al, C, Zn, Fe, Sn, Pb, H, Cu, Ag, Au, Pt

Quality factors
α 1-20

β = 1

γ, xray = 1

$n^0 = 3\text{-}10$

$p^+ = 1\text{-}10$

$1\ Sv = 1J/kg \cdot QF$

NUCLEAR CHEMISTRY
$E = mc^2$

$E^2 = m^2c^4 + p^2c^2$

∴ PHOTONS $E = pc$

Nuclear binding
$BE = (Zm_p + Nm_n - m_A)c^2$

coulomb pot
$V = \frac{q_1 q_2}{4\pi\epsilon_0 r} = \frac{9e9\,q_1q_2}{r}$

^{56}Fe most stable

Nuclear decay
alpha decay - paper

$^{238}_{92}U \rightarrow ^{234}_{90}Th + ^4_2He$

beta decay - Al

$^{14}_6C \rightarrow ^{14}_7N + ^0_{-1}e^- + \bar{\nu}$

positron emission

$^{11}_6C \rightarrow ^{11}_5B + ^0_1e^+ + \nu$ $\Delta m = m[^{11}_5B] + 2m[^0_1e^+] - m[^{11}_6C]$

electron capture

$^{231}_{92}U + ^0_{-1}e^- \rightarrow ^{231}_{91}Pa + \nu_e$

$p^+ + e^- \rightarrow n^0 + \nu_e$

gamma decay - Pb

→ gives off EM rad as photon

Kinetics
$A = -\frac{dN}{dt} = kN$

$A = A_0e^{-kt}$

$k = \ln 2/t_{1/2}$

$N = N_0e^{-kt}$

$k_{tot} = k_{bio} + k_{rad}$

conservation
- energy
- charge
- momentum
- lepton # $\nu_e, \bar{\nu}_e$
- baryon #

Fission
$^1_0n + ^{235}_{92}U \rightarrow ^{72}_{30}Zn + ^{162}_{62}Sm + 2^1_0n$

Fusion
$^1H + ^1H \rightarrow ^2H + ^0_1e^+ + \nu$

$^2H + ^1H \rightarrow ^3He + \gamma$

$^3_2He + ^3_2He \rightarrow ^4_2He + 2^1_1H$

Quantum mech
waves $\ddot{n}$

traveling $k = 2\pi/\lambda$ speed $= \lambda\nu$

$f(x,t) = A\sin(\omega t - kx)$ $c = \lambda\nu$ photons

standing $\nu = \frac{c}{\lambda}$ ∴ $E = h\nu = \frac{hc}{\lambda}$

$f(x,t) = 2A\sin(kx)\cos(\omega t)$

Energy quantization
$p(\lambda,T) = \frac{8\pi hc}{\lambda^5} \cdot \frac{1}{\exp\frac{hc}{\lambda k_BT} - 1}$

UV catastrophe = classical

Planck

- E = discrete, gain/lose ΔE in quanta
- to emit E, T sufficiently high

Frank-Hertz and V_{thr}
$\nu = \Delta E/h = \frac{eV_{thr}}{h}$

1e⁻ ionization $(2.18e\text{-}18J)\frac{Z^2}{\lambda^2}$

$E_n = \frac{Z^2}{n^2}\,ryd = 13.6\frac{Z^2}{n^2}\,eV$

EM rad
$E(x,t) = E_{max}\cos\left(2\pi\left(\frac{x}{\lambda}\right) - \nu t\right)$

- constructive/destructive interference

Light absorption
$\nu = \frac{E_f - E_0}{h}$ or $\Delta E = h\nu$

BOHR MODEL
$E = \frac{1}{2}m_ev^2 - \frac{Ze^2}{4\pi\epsilon_0 r} = $ kinetic + potential

Ang. momentum $= L = m_evr = nh/2\pi$

$r_n = \frac{n^2}{Z}a_0$ $v_n = \frac{nh}{2\pi m_e r_n} = \frac{Ze^2}{2\epsilon_0 nh}$

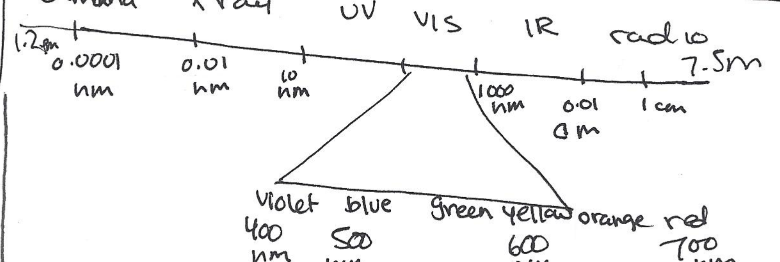
Atomic Spectra interpretation
$\nu = (3.29e15\ s^{-1})Z^2\left(\frac{1}{n_i^2} - \frac{1}{n_f^2}\right)$

Ratio of Decay
$\frac{N_{H^+}}{N_H} = e^{-\Delta E/k_BT}$ $\Delta E = 13.6\ eV$ (ionization)

Finding min λ
$KE = h\nu - \phi = \frac{1}{2}mv^2$ → $\lambda = \frac{h}{p}$

Double slit exp.
$\frac{n\lambda_1}{n\lambda_2} = \frac{d_1\sin\theta}{d_2\sin\theta}$ $\frac{\lambda_1}{\lambda_2} = \frac{d_1}{d_2}$

$\frac{E_2}{E_2} = \frac{d_1}{d_2}$ bc $E \propto \frac{1}{\lambda}$



Photoelectric effect
$E = h\nu$

$E_{max} = \frac{1}{2}m_ev^2 = h\nu - \phi = hc/\lambda - \phi$

$\phi = h\nu_0$ energy barrier must overcome

Schrödinger
$\psi^*\psi$ = probability $P = |\psi^2|dx$

particle in a small vol dV @ pt(x,y,z) @ time t

1D

$E\psi(x) = \frac{-h^2}{8\pi^2 m}\frac{d^2\psi(x)}{d^2(x)} + V(x)\psi(x)$

m: mass; V(x): PE func

PROBABILITY
- must be normalized $\int\psi(x)^2 = 1$
- ψ must be cont
- vertical line test

Normalize
$\int_a^b \frac{2}{L}\sin^2\left(\frac{2\pi x}{L}\right)dx$

$= \frac{2}{L}\left(\frac{x}{2} - \frac{L}{4\pi}\sin\left(\frac{4\pi x}{L}\right)\frac{1}{2}\right)\Big|_a^b$

De Broglie waves (standing wave)
$\lambda = h/m_ev = \frac{h}{p}$

Heisenberg kms
$\Delta x\Delta p \geq h/4\pi$

max V of pe @ 12.4nm

$E = hc/\lambda$ then $E = \frac{Z^2}{n^2}13.6eV$

$E_{KE} = E_{photon} - E_{ionization}$

Particle in a Box (needs to die)
1D

$\psi(x) = A\sin kx$

$\frac{d^2\psi(x)}{d^2(x)} = -\left(\frac{n\pi}{L}\right)^2\psi_x$

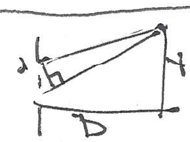
$E_n = \frac{n^2h^2}{8mL^2}$ $n = 1,2,3\ldots$

3 & 2D

$E = \frac{h^2}{8m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)$

Leptons	charge	lepton #
$^0_{-1}e^-, \beta^-$	-1	+1
$^0_1e^+, \beta^+$	+1	-1
ν_e	0	+1
$\bar{\nu}_e$	0	-1

Baryons	charge	bar #
$^1_1p^+$	+1	+1
$\bar{p}$	-1	-1
$^1_0n^0$	0	+1
$\bar{n}$	0	-1



$y = \frac{n\lambda D}{d}$

Irika Sinha
Chem 15S AB
1732892