CHEMISTRY 155 OCT/2002

PROBLEM SET 4

THE FOLLOWING 8 PROBLEMS ARE FROM GRAY p38-40. EACH PROBLEM HAS A VALUE OF 10pts.

PROBLEM ? HAS A VALUE OF 100pts.

Problem 4 (READ SEC 1-7 IN GRAY)

FOR H_2^+ THE NUCLEAR CHARGE IS EQUAL to $2|e|$ OR, IN GENERAL, $Z|e|$ WITH $Z_{H_2^+} = 2$. CONSEQUENTLY THE POTENTIAL ENERGY IS GIVEN BY

$$V = -\frac{Z|e|^2}{4\pi\epsilon_0 r} \quad (4\text{-}1)$$

WE NOTICE THAT THE DIFFERENCE BETWEEN THE POTENTIAL USED IN THE TEXTBOOK AND Eq. (4-1) IS DUE TO THE NUCLEAR CHARGE

$$|e|^2 \longrightarrow Z|e|^2 \quad (4\text{-}2)$$

WITH Eq. (4.2) WE CAN SUBSTITUE THE NUCLEAR CHARGE IN Eq (1-13) TO OBTAIN THE ENERGY LEVELS FOR ANY HYDROGEN LIKE ATOM

$$E_n = \frac{2\pi^2 m_e Z^2 |e|^2}{h^2} \frac{1}{n^2} \qquad (4\text{-}3)$$

FINALLY WE CAN USE Eq. (4-3) IN SECTION 1-5, IN PARTICULAR Eq. (1-15), AND OBTAIN AN EXPRESSION

$$\Delta E = \frac{2\pi^2 m_e Z^2 |e|^2}{h^2} \left[\frac{1}{n_I^2} - \frac{1}{n_{II}^2} \right] \qquad (4\text{-}4)$$

OR

$$\bar{\nu} = \frac{2\pi^2 m_e Z^2 |e|^4}{c h^3} \left[\frac{1}{n_I^2} - \frac{1}{n_{II}^2} \right] . \qquad (4\text{-}5)$$

IF WE USE THE BOHR VALUE OF THE RYDBERG CONSTANT,

$$R_H = \frac{2\pi^2 m_e |e|^4}{c h^3} , \qquad (4\text{-}6)$$

WE CAN REWRITE Eq (4-5) AS

$$\bar{\nu} = Z^2 R_H \left[\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right]. \qquad (4-7)$$

SINCE WE NEED THE WAVELENGTH, WE RECALL THE RELATION BETWEEN WAVENUMBER AND WAVELENGTH,

$$\bar{\nu} = \frac{1}{\lambda}.$$

THEREFORE THE WAVELENGTH IS GIVEN BY:

$$\lambda = \frac{1}{Z^2 R_H \left[\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right]}. \qquad (4-8)$$

FOR OUR PROBLEM $Z = 2$, $n_I = 3$ AND $n_{II} = 4$

$$\lambda_{4\to3} = \frac{1}{R_H}\frac{36}{7} = \frac{36}{7}\frac{ch^3}{2\pi^2 m_e |e|^4}$$

$$\boxed{\lambda_{4\to3} = \frac{18}{7}\frac{ch^3}{\pi^2 m_e |e|^4}}$$

FROM PAGE 14 IN GRAY, WE KNOW THE VALUE OF R_H,

$$R_H = 109\,677.581 / cm^{-1}$$

$$R_H = 1.09677581 \times 10^{7}\ m^{-1}.$$

THUS

$$\lambda_{4\to3} = \frac{36}{7}\,\frac{1}{1.09677581 \times 10^{7}\ m^{-1}}$$

$$\lambda_{4\to3} = 4.6891 \times 10^{-7}\ m$$

$$= 4689.1\ \mathring{A}$$

$$\boxed{\lambda_{4\to3} = 468.91\ nm}$$

VISIBLE GREEN REGION

PROBLEM 5

$\nu = 0.66 \times 10^{15}\ s^{-1}$

$E = h\nu = 6.6260688 \times 10^{-34}\ J\ s\ 0.66 \times 10^{15}\ s^{-1}$

$= 4.4 \times 10^{-19}\ J$ (2 sig figs)

$h = 6.6260688 \times 10^{-34}\ J\ s$

$h = 6.6260688 \times 10^{-27}\ erg\ s$

$1\ cal = 4.184\ J$

$1\ eV = 1.60217646 \times 10^{-19}\ J$

$1\ eV = 96.485342\ kJ\ mol^{-1}$

$1\ eV = 23.0606\ kcal\ mol^{-1}$

$E = 4.4 \times 10^{-19}\ J = 2.7\ eV$
$= 63\ kcal\ mol^{-1}$
$= 260\ kJ\ mol^{-1}$

Sig Figs 2

PROBLEM 8

a) FOR THIS PROBLEM WE SUGGEST THE FOLLOWING INITIAL TRANSITION

$$(1s)^2(2s)^1 \longrightarrow (1s)^2(2s)^0(2p)^1.$$

THE LIGHT OBSERVED AT 6708 Å IS DUE TO THE TRANSITION

$$(1s)^2(2s)^0(2p)^1 \longrightarrow (1s)^2(2s)^1\ (2p)^0$$

b) $c = \lambda\nu$

$$\nu = \frac{c}{\lambda} = \frac{2.99792458 \times 10^8\ m\,s^{-1}}{6.708 \times 10^{-7}\ m}$$

$$\text{Å} = 10^{-10}\ m$$

$$\boxed{\nu = 4.469 \times 10^{14}\ s^{-1}}$$

c) $$\bar{\nu} = \frac{1}{\lambda} = \frac{1}{6.708 \times 10^{-5}\ cm^{-1}} = 1.491 \times 10^{4}\ cm^{-1}$$

d) $$E = h\nu = \frac{hc}{\lambda} = \frac{19.8645 \times 10^{-26}\ J \cdot m}{6.708 \times 10^{-7}\ m}$$

$E = 2.961 \times 10^{-19}\ J = 1.848\ eV$

$E = 42.62\ kcal\ mol^{-1}$

PROBLEM 9

a) EXCITED ; POSSIBLE X-ray PHOTONS
b) FORBIDDEN ; ↑ ↑ IN 1S
c) GROUND
d) EXCITED ⊛ (FORBIDDEN)
e) EXCITED ; LOW PROBABILITY TOTAL SPIN IS NOT CONSERVED
f) SAME AS d)

⊛ THIS IS AN EXCITED STATE BUT THE TRANSITION TO THE GROUND STATE IS SPIN FORBIDDEN. ALSO THE TRANSITION ↑↑↑ → ↑↓ _ ↑ IS SPIN FORBIDDEN THUS IT IS AN EXTREMELY RARE EXCITED STATE

PROBLEM 13

3d →
$n = 3$
$l = 0, 1, 2$
$m = 0, \pm 1, \pm 2$

PROBLEM 17

$\bar{\nu}_1 = 329\ 170\ cm^{-1}$
$\bar{\nu}_2 = 399\ 020\ cm^{-1}$
$\bar{\nu}_3 = 411\ 460\ cm^{-1}$
$\bar{\nu}_4 = 421\ 330\ cm^{-1}$

PROBLEM 17

ASSUME

$$\bar{\nu}_i = R\left(\frac{1}{n_1^2} - \frac{1}{n_{i+1}^2}\right)$$

$n_i = 2, 3, 4, 5$

$n_1 = 1$

FOR $i = 1$

$$\bar{\nu}_1 = R\left[1 - \frac{1}{2^2}\right] = \frac{3}{4}R$$

OR

$$R = \frac{4}{3}\bar{\nu}_1 = 438\,890 \text{ cm}^{-1}$$

a) $$\bar{\nu}_2 = \frac{4}{3}\bar{\nu}_1\left[1 - \frac{1}{3^2}\right] = \frac{4}{3}\bar{\nu}_1 \frac{8}{9} = \frac{32}{27}\bar{\nu}_1$$

$$\Rightarrow \quad \frac{\bar{\nu}_2}{\bar{\nu}_1} = \frac{32}{27} = 1.1852$$

Exp $$\frac{\bar{\nu}_2^{Exp}}{\bar{\nu}_1^{Exp}} = 1.2122$$

b) $$\bar{\nu}_3 = \frac{4}{3}\bar{\nu}_1\left[1 - \frac{1}{16}\right] = \frac{4}{3}\bar{\nu}_1 \frac{15}{16}$$

$$\frac{\bar{\nu}_3}{\bar{\nu}_1} = \frac{60}{48} = 1.2500$$

Exp $$\frac{\bar{\nu}_3}{\bar{\nu}_1} = 1.2499$$

c) $\bar{\nu}_4 = \frac{4}{3}\bar{\nu}_1\left[1 - \frac{1}{5^2}\right] = \frac{4}{3}\bar{\nu}_1 \frac{24}{25}$

$$\frac{\bar{\nu}_4}{\bar{\nu}_1} = \frac{96}{75} = 1.2800$$

EXP $\frac{\bar{\nu}_4}{\bar{\nu}_1} = 1.2800$

THEREFORE THE DATA ARE CONSISTENT WITH THE FOLLOWING FORMULA

$$\bar{\nu}_n = R\left[1 - \frac{1}{(n+1)^2}\right]$$

OR

$$\bar{\nu} = R\left[\frac{1}{n_I^2} - \frac{1}{n_{II}^2}\right]$$

WHERE $n_I = 1$ AND $n_{II} = 2, 3, 4, 5$

d) VALUES OR R FROM DATA

$\frac{\bar{\nu}_1}{3/4} = 438\ 890\ cm^{-1}$	$\frac{\bar{\nu}_3}{15/16} = 438\ 890\ cm^{-1}$
$\frac{\bar{\nu}_2}{8/9} = 448\ 900\ cm^{-1}$	$\frac{\bar{\nu}_4}{24/25} = 438\ 890\ cm^{-1}$

$$\bar{R} = 441\ 390\ \text{cm}^{-1}$$

$$\frac{\bar{R}}{R_H} = 4.0244$$

THEORY PREDICTS $\frac{\bar{R}}{R_H} = 4.0000$

EXPERIMENTAL DATA ARE JUST 0.5% OFF

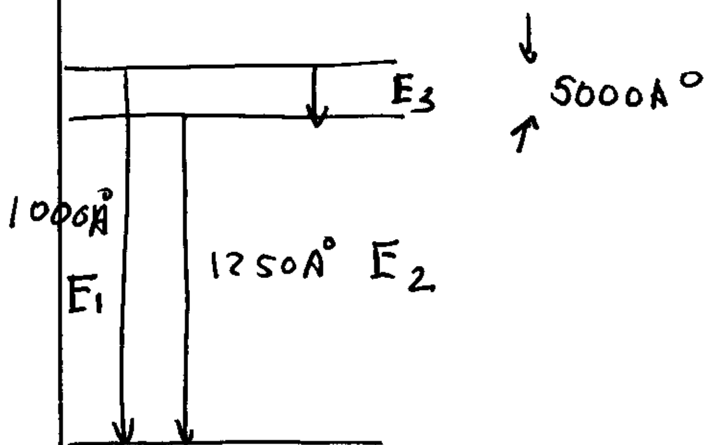
THE THEORETICAL VALUE.

PROBLEM 18

REMEMBER THAT

$$E = h\nu = \frac{hc}{\lambda}$$

THUS SHORTER WAVELENGTH IMPLIES GREATER ENERGY



TWO OF THE WAVELENGTHS ARE CLOSE TO EACHOTHER AND REPRESENT 2 TRANSITIONS

THE 5000 Å REPRESENTS A TRANSITION BETWEEN EXCITED STATES (FROM PROBLEM 8.- $hc = 19.8645 \times 10^{-26}$ J m)

$$E_1 = \frac{hc}{\lambda} = \frac{19.8645 \times 10^{-26} \text{ J m}}{10^3 \; 10^{-10} \text{ m}}$$

$$E_1 = 19.8645 \times 10^{-19} \text{ J} = 12.40 \text{ eV}$$

$$E_2 = 12.40 \text{ eV} \; \frac{1000}{1250} = 9.919 \text{ eV}$$

$$E_3 = 12.40 \text{ eV} \; \frac{1000}{5000} = 2.480 \text{ eV}$$

PROBLEM 19

THE SPLITTING OF THE 4s, 4p, 4d AND 4f level IN H IS DUE TO THE ELECTRON-ELECTRON INTERACTION IN MANY-ELECTRON ATOMS.