

average = 14.3
s.d. = 5.9

27
15-20 B
10 C
5 D
0 F

$c = 3 \times 10^8 \text{ m/sec}$
 $h = 6.626 \times 10^{-34} \text{ J sec}$
 $k_B = 1.38 \times 10^{-23} \text{ J/K}$
A
 $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}$
 $1 \text{ Watt} = 1 \text{ J/sec}$
 $1 \text{ nm} = 10^{-9} \text{ m}$
 $1 \text{ mm} = 10^{-3} \text{ m}$

Quiz # 1
Chem 4120/6120
June 12, 2008

Name: _____

(Closed book, but one 8.5 by 11 inch sheet of notes can be used.)

(5) 1. A lamp emits 1.0 Watt of light at a wavelength of 500 nm. Light is emitted in all directions with equal probability. The number of photons/second ($\lambda = 500 \text{ nm}$) emitted by the lamp, N, is

$$N = \frac{W}{h\nu} = \frac{W\lambda}{hc} = \frac{(1 \text{ J/sec})(500 \times 10^{-9} \text{ m})}{(6.626 \times 10^{-34} \text{ J sec})(3 \times 10^8 \text{ m/sec})} = 2.5 \times 10^{18} \frac{1}{\text{sec}}$$

- (a) 2.5×10^{-3} (b) 2.5×10^3 (c) 2.5×10^{12} (d) 2.5×10^{18}

(5) 2. For the lamp in the previous problem, suppose a detector (area = 1 mm^2) is placed at a distance of 1 m from the surface of the lamp. The number of photons ($\lambda = 500 \text{ nm}$) reaching the detector (N is total number emitted by lamp at this wavelength) is

$$n = N \left(\frac{A}{4\pi R^2} \right) = N \left(\frac{1 \text{ mm}^2}{4\pi (1000 \text{ mm})^2} \right) = 7.96 \times 10^{-8} N$$

- (a) $7.96 \times 10^{-8} N$ (b) $1.0 \times 10^{-6} N$ (c) $1.0 \times 10^{-3} N$ (d) N

(5) 3. Which statement below about blackbody radiation is not true?

- (a) it corresponds to equilibrium between emission & absorption of radiation *true*
(b) it is independent of the composition of the radiation source *true*
(c) the intensity of radiation increases as $(1/\lambda)^2$ at a particular temperature *this is "uv catastrophe"*
(d) the wavelength maxima decreases with increasing temperature *true*

(5) 4. A heated body is assumed to obey the blackbody distribution law. At a temperature of 1500 K, what wavelength (in nm) is the emission spectrum of the body at a maximum?

$$\lambda_{\text{max}} \approx \frac{hc}{5k_B T} = \frac{(6.626 \times 10^{-34} \text{ J sec})(3 \times 10^8 \text{ m/sec})}{(5)(1.38 \times 10^{-23} \text{ J/K})(1500 \text{ K})} = 1.920 \times 10^{-6} \text{ m}$$

- (a) 45 (b) 1030 (c) 1920 (d) 7850

(5) 5. The Bohr model predicts that an electron in the ground state ($n = 1$) of a hydrogen atom orbits the nucleus at a distance of 0.053 nm. For an electron in the $n = 3$ level, the orbital radius (in nm) would be

$$r = a_0 n^2 / Z = (0.053)(9)/1 = 0.477 \text{ nm}$$

- (a) 0.0059 (b) 0.159 (c) 0.477 (d) 1.54

(5) 6. Light of wavelength 420 nm is required to cause photoelectrons to be ejected from a particular metal surface. If light of wavelength 350 nm strikes the metal surface, the kinetic energy of the emitted photoelectrons (in eV) will be

- (a) no photoelectrons (b) 0.59 (c) 1.28 (d) 2.47

$$h\nu = h\nu_0 + E$$

$$E = \frac{hc}{\lambda} - \frac{hc}{\lambda_0} = hc \left(\frac{1}{\lambda} - \frac{1}{\lambda_0} \right) = \frac{(6.626 \times 10^{-34} \text{ J s})(3 \times 10^8 \frac{\text{m}}{\text{sec}})}{(1.602 \times 10^{-19} \frac{\text{J}}{\text{eV}})} \left(\frac{1}{350 \times 10^{-9}} - \frac{1}{420 \times 10^{-9}} \right)$$

0.59 eV

a b
1 1
2 2
3 3
4 4
5 5
6 6

ave = 20.0
s.d = 6.6

Quiz #2
Chem 4120/6120
June 17, 2008

- A 27-30
- B 18-26
- C 13-17
- D 7-12
- F ≤ 6

$$\cos(a \pm b) = \cos a \cos b \mp \sin a \sin b$$

A

Name: _____

(Closed book, but one 8.5 by 11 inch sheet of notes can be used.)

The next three questions concern a traveling wave defined by $\Psi(x, t) = 3 \cos(2x - 5t)$ where x is in cm and t is in seconds.

(5) 1. The wavelength, λ (in cm) is

$$2 = \frac{2\pi}{\lambda} \Rightarrow \lambda = \frac{2\pi}{2} = \pi \approx 3.14$$

- (a) 0.5 (b) 1.0 (c) 2.0 (d) 3.14

(5) 2. The speed of the wave, v , in cm/sec, is

$$2x - 5t = 2vt - 5t = (2v - 5)t = \text{const}$$

- (a) 0.4 (b) 2.5 (c) 5.0 (d) speed of light

$$\therefore v = \frac{5}{2} = 2.5 \frac{\text{cm}}{\text{sec}}$$

(5) 3. Suppose we superimpose another traveling wave defined by

$\Phi(x, t) = 3.0 \cos(2x + 5t)$ onto $\Psi(x, t)$ above. The resulting wave can be written

- (a) $6 \cos(2x) \cos(5t)$ (b) $6 \sin(2x) \sin(5t)$
(c) $6 \cos(2x - 5t)$ (d) $6 \cos(2x)$

$$3 \cos(2x + 5t) + 3 \cos(2x - 5t) \\ = 3 \cos 2x \cos 5t - 3 \sin 2x \sin 5t \\ + 3 \cos 2x \cos 5t + 3 \sin 2x \sin 5t$$

(5) 4. The product of $(5-i)$ and $(3+2i)$ is

- (a) $13 + 7i$ (b) $17 + 7i$ (c) $15 - 2i$ (d) 17

$$(5-i)(3+2i) = 15 - 3i + 10i - 2i^2 = 17 + 7i$$

$$= 6 \cos 2x \cos 5t$$

(10) 5. Determine in each of the following cases if the function in the first column is an eigenfunction of the operator in the second column. (Circle the function in the first column if it is an eigenfunction - 2pts each.)

x^3 d/dx

$$\frac{d}{dx} x^3 = 3x^2$$

xy $x(\partial/\partial x) + y(\partial/\partial y)$

$$x \frac{\partial(xy)}{\partial x} + y \frac{\partial(xy)}{\partial y} = xy + yx = 2xy$$

$\sin \theta \cos \phi$ $\partial^2/\partial \theta^2$

$$\frac{\partial^2}{\partial \theta^2} (\sin \theta \cos \phi) = \cos \theta \frac{\partial^2}{\partial \theta^2} \sin \theta = -\sin \theta \cos \phi$$

$\exp(-x^2/2)$ $d^2/dx^2 - x^2$

$$\frac{d^2}{dx^2} e^{-4i\phi} = -4i \frac{d}{d\phi} e^{-4i\phi} = (4i)^2 e^{-4i\phi} = -16 e^{-4i\phi}$$

$\exp(-4i\phi)$ $d^2/d\phi^2$

$$\frac{d^2}{dx^2} e^{-x^2/2} = x^2 e^{-x^2/2} - \frac{d}{dx} (x e^{-x^2/2}) - x^2 e^{-x^2/2} = -x \frac{d}{dx} (e^{-x^2/2}) - e^{-x^2/2} = -x(-x) e^{-x^2/2} - e^{-x^2/2} = -e^{-x^2/2}$$

ave = 18
s.d. = 6.7

A 25-30
B 16-25
C 11-15
D < 11

Quiz # 3
Chem 4120/6120
June 19, 2008

A

Name: _____

(Closed book, but one 8.5 by 11 inch sheet of notes can be used.)

1. (8 pts) On the basis of the First Postulate of quantum mechanics, which function(s) below represent possible solutions, within a normalization constant, on the interval $-\infty < x < +\infty$? (Circle the possible solutions. More than one might be possible.)

- (a) $1/x$ (b) x^2 (c) $\exp(-ax)$ (d) $\exp(-ax^2)$
- diverge at x=0* *diverge at -∞*

2. (5 pts) Consider the equation, $\Psi(x, t) = A \exp[+i(kx - \omega t)]$ where A is a constant. Is $\Psi(x, t)$ an eigenfunction of \hat{p} and if so, what is the eigenvalue?

- (a) no (b) yes, 1 (c) yes, $+\hbar k$ (d) yes, $-\hbar k$

$\hat{p} = -i\hbar \frac{d}{dx}$
 $\hat{p} \Psi = -i\hbar \frac{d}{dx} [A e^{i(kx - \omega t)}] = -i\hbar(i k) A e^{i(kx - \omega t)} = +\hbar k \Psi$

3. (5 pts) Is $\Psi(x, t) = A \exp[+i(kx - \omega t)]$ an eigenfunction of the kinetic energy operator, \hat{K} and if so, what is the eigenvalue? (m is the particle mass)

- (a) no (b) yes, $+\hbar k^2$ (c) yes, $-\hbar k^2$ (d) yes, $+\hbar k^2/(2m)$

$\hat{K} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$
 $\hat{K} \Psi = -\frac{\hbar^2}{2m} (-k^2 \Psi) = +(\hbar^2 k^2 / 2m) \Psi$

4. (6 pts) Assume ϕ_1 and ϕ_2 are normalized and orthogonal eigenfunctions of the operator A with eigenvalues a_1 and a_2 , respectively. Suppose we prepare a system in state $\psi = N(\phi_1 + \phi_2)$ where N is a normalization constant. What must N be in order that ψ is normalized?

- (a) $1/2$ (b) $1/\sqrt{2}$ (c) 1 (d) 2

$c_1 = N, c_2 = N, \text{ all other } c_i = 0$
 $1 = \sum_j c_j^* c_j = c_1^2 + c_2^2 = N^2 + N^2 = 2N^2$
 $\therefore N = \pm 1/\sqrt{2}$

5. (6 pts) Suppose 1000 measurements of A were carried out for a system prepared in state ψ of the previous problem. What would you measure?

- (a) All measurements would yield a_1
(b) All measurements would yield $(a_1 + a_2)/2$
(c) Roughly half would yield a_1 and the other half a_2
(d) A continuous distribution of values between a_1 and a_2

From postulate 3, must measure an eigenvalue in a single measurement. From post. 4) a few problems.
 $\langle a \rangle = \sum_j c_j^* c_j a_j = \frac{1}{2}(a_1 + a_2)$

A B
1 1
2 2
3 3
4 4
5 5

avg = 16
s.d. = 6

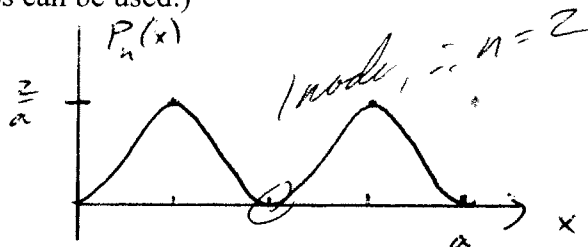
A 25-30
B 15-20
C 10
D ~~15~~ 5
E 0
Quiz # 4
Chem 4120/6120
June 24, 2008

A

Name: _____

(Closed book, but one 8.5 by 11 inch sheet of notes can be used.)

1. (5 pts) Plotted at right is $P_n(x)$ for a particle in a one dimensional box. What is n ?



- (a) 2 (b) 3 (c) 4 (d) 5

2. (5 pts) A particle in a one dimensional box of length a is in state $\phi_3(x) = \sqrt{2/a} \sin(3\pi x/a)$. The probability of finding the particle between $x = 0.31a$ and $x = 0.35a$ is

- (a) -0.125 (b) 0.001 (c) 0.125 (d) 0.250

$P_3 \approx \phi_3^* \phi_3 dx \approx \frac{2}{a} \sin^2\left(\frac{3\pi}{a} \left(\frac{a}{3}\right)\right) dx$

3. (5 pts) Suppose we prepared a particle in a box in state $\Psi(x) = N(\phi_1(x) - 3\phi_2(x))$ where the ϕ_j 's are energy eigenfunctions ($E_j = h^2 j^2 / (8 m a^2)$ where a is the length of the box. What is the normalization constant, N ?

- (a) $1/\sqrt{10}$ (b) $1/\sqrt{6}$ (c) $1/\sqrt{3}$ (d) $1/\sqrt{2}$

$c_1 = N, c_2 = -3N, \text{ all other } c_i = 0$
 $1 = N^2 + 9N^2 = 10N^2$

4. (5 pts) Repeated measurements of the energy of a particle prepared in the state described in the previous problem would yield

- (a) the same value every time
(b) E_1 33% of the time and E_3 67% of the time
(c) E_1 10% of the time and E_3 90% of the time
(d) a continuous range of values between E_1 and E_3

(If they answer (c) to (3), give them credit if they answer)

5. (5 pts) What is the solution for the time dependent Schrodinger equation, $\Psi(x, t)$, for the total energy eigenfunction, $\phi_3(x) = \sqrt{2/a} \sin(3\pi x/a)$?

- (a) $\phi_3(x)$ (b) $\phi_3(x) \sin(E_3 t/\hbar)$ (c) $\phi_3(x) \cos(E_3 t/\hbar)$ (d) $\phi_3(x) \exp(-i E_3 t/\hbar)$

$\Psi(x, t) = \phi_n(x) e^{-i E_n t/\hbar}$

6. (5 pts) For a particle in a 2-dimensional box of length "a" and width "b", the energy eigenfunctions can be written $\phi_{j,k}(x, y) = N \sin(j \pi x / a) \sin(k \pi y / b)$ where j and k are integers (j ranges from 1 to ∞ , k ranges from 1 to ∞). To insure proper normalization, what is N ?

- (a) 1 (b) $\sqrt{2/(ab)}$ (c) $2/\sqrt{ab}$ (d) $2/ab$

$1 = N^2 \int_0^a dx \int_0^b dy \sin^2\left(\frac{j\pi x}{a}\right) \sin^2\left(\frac{k\pi y}{b}\right) = N^2 \left(\frac{a}{2}\right) \left(\frac{b}{2}\right)$
So $N^2 = \frac{4}{ab} \Rightarrow N = \frac{2}{\sqrt{ab}}$

Quiz # 4
Chem 4120/6120
June 24, 2008

B

Name: _____

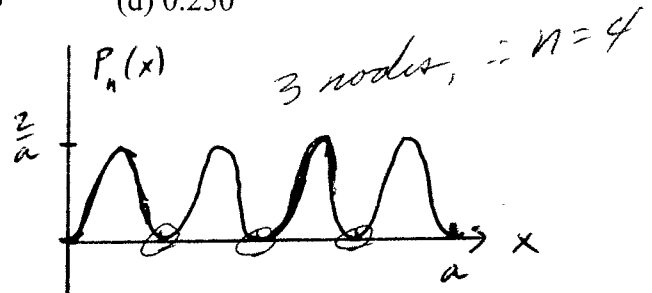
(Closed book, but one 8.5 by 11 inch sheet of notes can be used.)

1. (5 pts) A particle in a one dimensional box of length a is in state $\phi_3(x) = \sqrt{2/a} \sin(3\pi x/a)$. The probability of finding the particle between $x = 0.31a$ and $x = 0.35a$ is

- (a) -0.125 (b) 0.001 (c) 0.125 (d) 0.250

2. (5 pts) Plotted at right is $P_n(x)$ for a particle in a one dimensional box. What is n ?

- (a) 2 (b) 3 (c) 4 (d) 5



3. (5 pts) What is the solution for the time dependent Schrodinger equation, $\Psi(x, t)$, for the total energy eigenfunction, $\phi_3(x) = \sqrt{2/a} \sin(3\pi x/a)$? (E_3 is the energy.)

- (a) $\phi_3(x)$ (b) $\phi_3(x) \sin(E_3 t/\hbar)$ (c) $\phi_3(x) \cos(E_3 t/\hbar)$ (d) $\phi_3(x) \exp(-i E_3 t/\hbar)$

4. (5 pts) Suppose we prepared a particle in a box in state $\Psi(x) = N(\phi_1(x) - 3\phi_2(x))$ where the ϕ_j 's are energy eigenfunctions ($E_j = \hbar^2 j^2 / (8 m a^2)$ where a is the length of the box. What is the normalization constant, N ?

- (a) $1/\sqrt{10}$ (b) $1/\sqrt{6}$ (c) $1/\sqrt{3}$ (d) $1/\sqrt{2}$

5. (5 pts) Repeated measurements of the energy of a particle prepared in the state described in the previous problem would yield

- (a) the same value every time
(b) E_1 33% of the time and E_3 67% of the time
(c) E_1 10% of the time and E_3 90% of the time
(d) a continuous range of values between E_1 and E_3

6. (5 pts) For a particle in a 2-dimensional box of length " a " and width " b ", the energy eigenfunctions can be written $\phi_{j,k}(x, y) = N \sin(j \pi x / a) \sin(k \pi y / b)$ where j and k are integers (j ranges from 1 to ∞ , k ranges from 1 to ∞). To insure proper normalization, what is N ?

- (a) 1 (b) $\sqrt{2/(ab)}$ (c) $2/\sqrt{ab}$ (d) $2/ab$

ave = 18
s.d = 7

A = 25-30
B = 16-24
C = 11-15
D = 5-10
E < 5

Quiz # 5
Chem 4120/6120
June 26, 2008

$h = 6.626 \times 10^{-34} \text{ J scc}$
 $m_e = 9.11 \times 10^{-31} \text{ kg}$
 $c = 3 \times 10^8 \text{ m/scc}$
 $1 \text{ nm} = 10^{-9} \text{ m}$
A

Name: _____

(Closed book, but one 8.5 by 11 inch sheet of notes can be used.)

This quiz concerns modeling the conjugated pi electrons of 1,3 butadiene, (CH₂=CH-CH=CH₂), 1,3,5 hexatriene (CH₂=CH-CH=CH-CH=CH₂), and 1,3,5,7 octatetraene ((CH₂=CH-CH=CH-CH=CH-CH=CH₂). Each are modeled as a 1 dimensional particle in a box of length a. Take C=C and C-C bond lengths to be 0.135 and 0.154 nm, respectively. You can assume the pi electrons are free to move over the entire length of the molecule, but not beyond. Let E_n denote the n-th particle in a box energy.

$a(1,3) = 2 * .135 + .154 = .424 \text{ nm}$
 $a(1,3,5) = 3 * .135 + 2 * .154 = .424 + (.135 + .154) = .713 \text{ nm}$

1. (5pts) The box lengths, a, for 1,3 butadiene and 1,3,5 hexatriene (in nm) are:

- (a) .135, .154 (b) .154, .135 (c) .424, .713 (d) .713, .424

2. (5 pts) Assuming 2 pi electrons can go into a single particle-in-a-box energy level, the energy of the HOMO and LUMO levels of 1,3 butadiene are (4 pi electrons)

- (a) E₁, E₂ (b) E₂, E₃ (c) E₃, E₄ (5) E₄, E₅

4
3
2
1

3. (5 pts) Repeat the above question for 1,3,5 hexatriene (6 pi electrons)

- (a) E₁, E₂ (b) E₂, E₃ (c) E₃, E₄ (5) E₄, E₅

4. (8 pts) The wavelength of light (in nm) required to promote an electron from the HOMO to LUMO levels of 1,3,5,7 octatetraene would be

$a = .713 + .289 = 1.002 \text{ nm}$

- (a) 147 (b) 368 (c) 452 (d) 628

5. (7 pts) Suppose you had a homologous series of conjugated pi molecules such as those considered above. What would you expect to happen to the wavelength absorption maxima, λ_{max}, as the degree of conjugation increases?

- (a) λ_{max} decreases (b) λ_{max} increases (c) no change (d) depends on the series

$\lambda_{max} \propto \frac{a^2}{(n_{LUMO} - n_{HOMO})^2} \propto \frac{n^2}{(n+1)^2 - n^2} \approx \frac{n^2}{2n+1} \approx n$

$h\nu = \frac{hc}{\lambda} = E_{LUMO} - E_{HOMO} = \frac{h^2}{8ma^2} (n_{LUMO}^2 - n_{HOMO}^2)$
 $\lambda = \frac{8ma^2c}{h} (n_{LUMO}^2 - n_{HOMO}^2)^{-1} = \frac{8(9.11 \times 10^{-31})(1.002 \times 10^{-9})^2(3 \times 10^8)}{(6.626 \times 10^{-34})(25-19)}$
 $= 3.68 \times 10^{-7} \text{ m} = 368 \text{ nm}$

Quiz # 5
Chem 4120/6120
June 26, 2008

B

Name: _____

(Closed book, but one 8.5 by 11 inch sheet of notes can be used.)

This quiz concerns modeling the conjugated pi electrons of 1,3 butadiene, $(\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2)$, 1,3,5 hexatriene $(\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2)$, and 1,3,5,7 octatetraene $(\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2)$. Each are modeled as a 1 dimensional particle in a box of length a . Take C=C and C-C bond lengths to be 0.135 and 0.154 nm, respectively. You can assume the pi electrons are free to move over the entire length of the molecule, but not beyond. Let E_n denote the n -th particle in a box energy.

1. (5pts) The box lengths, a , for 1,3,5 hexatriene and 1,3 butadiene (in nm) are:

(a) .135, .154 (b) .154, .135 (c) .424, .713 (d) .713, .424

2. (5 pts) Assuming 2 pi electrons can go into a single particle-in-a-box energy level, the energy of the HOMO and LUMO levels of 1,3,5 hexatriene

(a) E_1, E_2 (b) E_2, E_3 (c) E_3, E_4 (d) E_4, E_5

3. (5 pts) Repeat the above question for 1,3 butadiene

(a) E_1, E_2 (b) E_2, E_3 (c) E_3, E_4 (d) E_4, E_5

4. (8 pts) The wavelength of light (in nm) required to promote an electron from the HOMO to LUMO levels of 1,3,5,7 octatetraene would be

(a) 147 (b) 368 (c) 452 (d) 628

5. (7 pts) Suppose you had a homologous series of conjugated pi molecules such as those considered above. What would you expect to happen to the wavelength absorption maxima, λ_{max} , as the degree of conjugation decreases?

(a) λ_{max} ~~increases~~ ^{decreases} (b) λ_{max} increases (c) no change (d) depends on the series

~~1,3 butadiene 1,3,5 hexatriene~~

$mc = 18 \pm 6$

- 16-23 B
- 12-15 C
- 6-11 D
- 0-5 F

$h = 6.626 \times 10^{-34} \text{ J sec}$
 $c = 3 \times 10^8 \text{ m/sec}$
 $N_{AV} = 6.02 \times 10^{23}$
 $r_m = 100 \text{ cm}$
 $r = 10^{19} \text{ nm}$

Quiz # 6
Chem 4120/6120
July 1, 2008

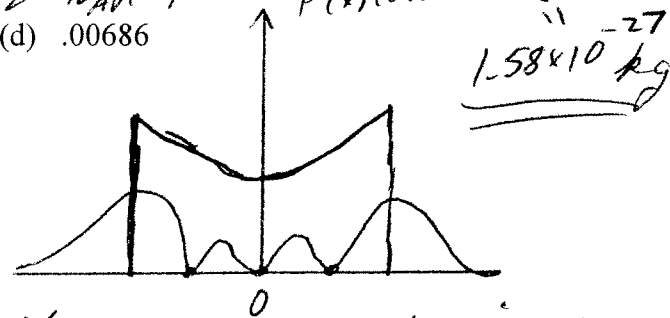
Name: _____

(Closed book, but one 8.5 by 11" sheet of notes can be used.)

(5) 1. The molar masses of H and F are .001 and .019 kg/mole, respectively. The reduced mass, μ (in kg), of a single HF molecule is $\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{M_1 M_2}{N_{AV}(M_1 + M_2)} = \frac{(.001)(.019)}{(6.02 \times 10^{23})(.020)}$

(a) 1.58×10^{-27} (b) 1.14×10^{-26} (c) .001 (d) .00686

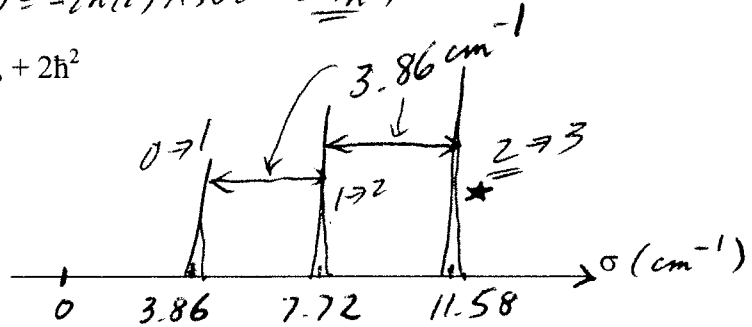
(5) 2. Plotted at right is the probability distribution of a classical harmonic oscillator versus x with energy $\epsilon = 7h\nu/2$. Superimpose on this the probability distribution of a quantum oscillator with $v = 3$ (same energy as above). Your plot does not have to be exact, but should be qualitatively correct.



(4) 3. Consider $\Psi(\theta, \phi) = A \sin\theta e^{i\phi}$. Is this an eigenfunction of L_z ? If so, what is the eigenvalue?

(a) no (b) yes, $-\hbar$ (c) yes, $+\hbar$ (d) yes, $+2\hbar^2$

(5) 4. Shown at right is the microwave spectrum of CO (absorbance versus wavenumber, σ (in cm^{-1})). The peak denoted by * corresponds to which initial rotational level, J ?



(a) 0 (b) 2 (c) 3 (d) 4

(7) 5. On the basis of the above figure, the bond length of CO (in nm) is

(a) 0.113 (b) 0.127 (c) 0.343 (d) 1.13

$\mu_{CO} = \frac{(.012)(.016)}{(6.02 \times 10^{23})(.028)} = 1.14 \times 10^{-26} \text{ kg}$

(4) 6. The IR spectrum of CO provides what useful information about its structure?

(a) stretching force constant (b) molecular polarizability
(c) bond length (d) both (a) and (c)

$2B = 3.86 \text{ cm}^{-1} = \frac{h}{4\pi^2 c \mu r_0^2} \Rightarrow r_0^2 = \frac{h}{4\pi^2 c \mu (2B)} = \frac{6.626 \times 10^{-34} \text{ J sec}}{(39.478)(3 \times 10^8 \frac{\text{m}}{\text{sec}})(1.14 \times 10^{-26} \text{ kg})}$
 $= 1.271 \times 10^{-20} \text{ m}^2$
 $r_0 = 1.13 \times 10^{-10} \text{ m} = 113 \text{ pm}$

$ave = 16 \pm 6$

- A 22-30
- B 14-21
- C 10-13
- D 4-9

Quiz # 7
 Chem 4120/6120
 July 8, 2008

A

Name: _____

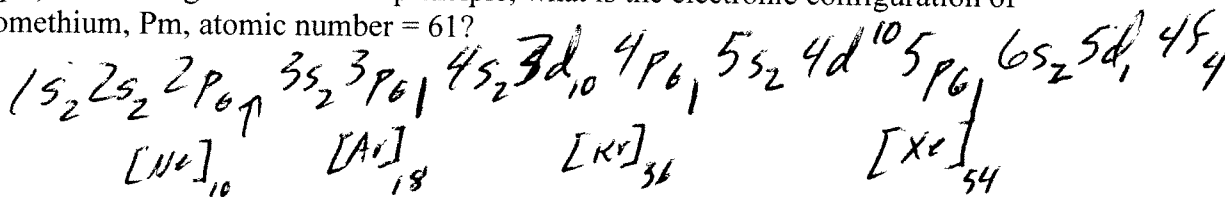
(Closed book, but one 8.5 by 11 inch sheet of notes can be used.)

- (5 pts) It is impossible to solve the time independent Schrodinger Equation of Helium exactly because
 - The Born-Oppenheimer Approximation does not apply in this case.
 - It is impossible to write down an exact Hamiltonian.
 - The electron-electron repulsion term makes the problem unsolvable.
 - The nuclear charge is too large.
- (5 pts) For H, the average distance of an electron from the nucleus in the ground electronic state, $\langle r \rangle_{1s}$, is $3a_0/2$ where a_0 is the Bohr radius. What is $\langle r \rangle_{1s}$ for Li^{+2} ?

- (a) $a_0/9$ (b) $a_0/2$ (c) $3 a_0/2$ (d) $9 a_0$

$\langle r \rangle_{1s} = \frac{3}{2} \left(\frac{a_0}{Z} \right) = a_0/2$

- (7 pts) According to the Aufbau principle, what is the electronic configuration of Promethium, Pm, atomic number = 61?



- (6 pts) The first ionization energy of Boron (atomic number = 5) is 8.3 eV. The effective charge, Z_{eff} (in units of the protonic charge), seen by the outermost electron is

- (a) 1.00 (b) 1.56 (c) 2.43 (d) 4.00

$I = 27.2 \left(\frac{Z_{eff}^2}{n^2} \right) = \frac{27.2}{2^2} Z_{eff}^2$

$Z_{eff}^2 = 2.44$
 $Z_{eff} = 1.56$

- (7 pts) Consider the term symbols: $^1S_0, ^3S_1, ^3P_2, ^3P_1, ^1D_2, ^3D_2, ^3G_5$ corresponding to a particular Aufbau electronic configuration. You can assume the valence orbital is less than half full. According to Hund's Rules, the energy of these states in order of increasing energy is

- (a) $^1S_0 < ^3S_1 < ^3P_2 < ^3P_1 < ^1D_2 < ^3D_2 < ^3G_5$
 (b) $^3D_2 < ^3G_5 < ^3S_1 < ^3P_2 < ^3P_1 < ^1S_0 < ^1D_2$
 (c) $^3G_5 < ^3D_2 < ^3P_2 < ^3P_1 < ^3S_1 < ^1D_2 < ^1S_0$
 (d) $^3G_5 < ^3D_2 < ^3P_1 < ^3P_2 < ^3S_1 < ^1D_2 < ^1S_0$

① terms of highest S lie lowest
 ② terms of highest L lie lowest
 ③ lower J states lie lowest (if orbital less than half full).

$unc = 16 \pm 7$

$A = 25 - 13$
 $B = 15 - 20$

Quiz # 8

Chem 4120/6120

July 17, 2008

C 10
 D 5

$k_B = 1.38 \times 10^{-23} \frac{J}{K}$

$h = 6.626 \times 10^{-34} J \cdot sec$

$J = kg \cdot m^2 / sec^2$

$10m = 10^{-2} m$

Name: _____

(Closed book, but one 8.5 by 11 inch sheet of notes can be used.)

1. (5) Suppose you draw a card from a standard deck of 52 cards which contains 13 cards of each suit (clubs, spades, diamonds and hearts). The probability of selecting a card from a particular suit (a diamond, for example) is

- (a) ~~0.012~~ (b) 0.0192 (c) .0417 (d) .250
 4.95×10^{-4}

$P = \frac{13}{52} = 0.25$

2. (5) The probability of drawing 5 cards from a standard deck that are all of the same suit (this is called a "flush") is

- (a) ~~0.012~~ (b) 0.0192 (c) .0417 (d) .250
 4.95×10^{-4}

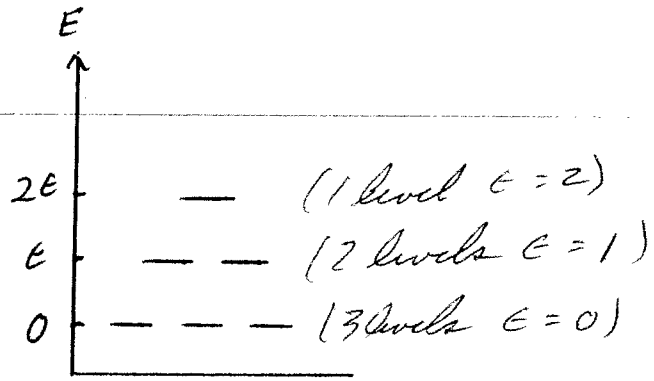
$P = \left(\frac{13}{52}\right) \left(\frac{12}{51}\right) \left(\frac{11}{50}\right) \left(\frac{10}{49}\right) \left(\frac{9}{48}\right)$
 ↑ first card ↑ second ↓ ↓ ↓ -4
 4.95×10^{-4}

3. (5) Consider the 7 letters Q, U, A, N, T, U, M. The number of different letter combinations you could write down from these seven letters is

- (a) 1 (b) 7! (c) $7!/2$ (d) $7!/(2!5!)$
(7 letters, but 2 are distinguishable)

4. (5) Consider the energy level distribution shown at right. The temperature is T and $\beta = 1/k_B T$. The partition function, Q, is

- (a) 1
 (b) $1 + e^{-\beta\epsilon} + e^{-2\beta\epsilon}$
 (c) $1 + 2e^{-\beta\epsilon} + e^{-2\beta\epsilon}$
 (d) $3 + 2e^{-\beta\epsilon} + e^{-2\beta\epsilon}$



5. (5) At very high temperature, the average energy for a particle from the previous problem would be

- (a) 0 (b) $2\epsilon/3$ (c) ϵ (d) 2ϵ

$\langle E \rangle = \frac{1}{6} (3 \cdot 0 + 2 \cdot \epsilon + 1 \cdot (2\epsilon))$
 $= \frac{4\epsilon}{6} = \frac{2}{3} \epsilon$

6. (5) How many "accessible states" does a Helium atom have which is confined to a 1 dimensional particle in a box of length $a = 1$ cm and $T = 298$ K? (The atomic weight of Helium is .004 kg/mole.)

- (a) 3.56×10^{-7} (b) 1.56 (c) 1.98×10^8 (d) 7.73×10^{24}

$g = a \left(\frac{2\pi m k_B T}{h^2} \right)^{1/2} = (10^{-2} m) \left(\frac{(6.28)^2 (0.004 kg / 23) (1.38 \times 10^{-23} J/K) (298 K)}{(6.626 \times 10^{-34} J \cdot sec)^2} \right)^{1/2}$

ave = 17 ± 5

- A 25-30
- B 15-20
- C 10
- D 5
- F 0

$R = 8.314 \text{ J/mol K}$
 $k_B = 1.381 \times 10^{-23} \text{ J/K}$
 $h = 6.626 \times 10^{-34} \text{ J s}$
 $N_{AV} = 6.02 \times 10^{23}$
 A $J = \text{kg m}^2/\text{sec}^2$

Quiz # 9
Chem 4120/6120
July 22, 2008

Name: _____

(Closed book, but one 8.5 by 11 inch sheet of notes can be used.)

This quiz concerns NO gas at 20 °C. Let q_{el} , q_{vib} , q_{rot} , and q_{trans} denote the single molecule partition functions associated with electronic, vibrational, rotational, and translational states. You are provided with the following information: Molecular Weight = 30 gm/mol, degeneracy of ground electronic state = 2, bond dissociation energy, D_0 , = 628 kJ/mole, vibrational temperature, θ_v , = 2719 K, rotational temperature, θ_r , = 2.45 K.

1) (5 pts) What is q_{el} ? $q_{el} = \sum_{el} e^{-D_0/RT} = 2e^{-(6.28 \times 10^5)/(8.314)(293.15)}$
 $= 2e^{-258} = 2 \times 10^{-112}$

(a) 2×10^{-112} (b) 2 (c) 3×10^{15} (d) $2 \times 10^{+112}$

2) (5 pts) What fraction of NO molecules are in the $v = 1$ vibrational level? (The lowest energy vibrational level is $v = 0$.)
 $p_1 = \frac{e^{-\frac{1}{2}\theta_v/T}}{e^{-\frac{1}{2}\theta_v/T} + e^{-\frac{3}{2}\theta_v/T} + e^{-\frac{5}{2}\theta_v/T}} \approx e^{-\frac{\theta_v}{2T}} (1 - e^{-\frac{\theta_v}{2T}})^{-1}$
 $e^{-\frac{\theta_v}{2T}} = e^{-\frac{2719}{2 \times 293}} = 9.28 \times 10^{-5}$

(a) 9.4×10^{-5} (b) 9.4×10^{-4} (c) .037 (d) .9999

3) (5 pts) What is q_{rot} ? $q_{rot} = T/\theta_r = 120$

(a) 9.66×10^{-3} (b) 60 (c) 120 (d) 3.56×10^7

4) (5 pts) What is q_{trans}/V where V is the container volume? (In this problem, you need to be careful about units!)
 $\frac{q_{trans}}{V} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} = \left(\frac{2\pi M R T}{N_{AV} h^2}\right)^{3/2} = \left(2.89 \times 10^{21} \frac{\text{kg J}}{\text{J}^2 \text{m}^2} \frac{\text{J sec}^2}{\text{kg m}^2}\right)^{3/2}$

(a) 1.5×10^8 (b) $3.7 \times 10^{19} \text{ m}^{-3}$ (c) $1.43 \times 10^{+32} \text{ kg/sec}^2$ (d) $1.43 \times 10^{+32} \text{ m}^{-3}$

5) (5 pts) The average thermodynamic energy/mole (in kJ/mole)?
 $-N_{AV} D_0 + \frac{5}{2} RT = -628 + \frac{5}{2} (-0.08314)(293.15) = -628 + 6 = -622$

(a) -634 (b) -628 (c) -622 (d) +622

6) (5 pts) What is the molar heat capacity at constant pressure, C_p , in J/mole K?

(a) 12.47 (b) 20.79 (c) 29.10 (d) 37.41

$C_p = C_v + R = \frac{5}{2} R + R = \frac{7}{2} R = 29.1 \frac{\text{J}}{\text{mole K}}$

ave = 15 ± 5

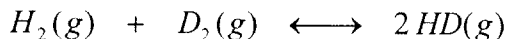
$N_{AV} = 6.02 \times 10^{23}$
 $k_B = 1.38 \times 10^{-23} \text{ J/K}$
 $R = 8.314 \text{ J/mole K}$
 $M_H = .001 \text{ kg/mole}$
 $M_D = .002 \text{ kg/mole}$

Quiz # 10
Chem 4120/6120
July 24, 2008

Name: _____

(Closed book, but one 8.5 by 11 inch sheet of notes can be used.)

This quiz concerns the deuterium (D) isotope reaction



You are given: $D_0(H_2) = 464 \text{ kJ/mole}$, $\theta_v(H_2) = 6210 \text{ K}$, $\theta_r(H_2) = 85.4 \text{ K}$. Also let R_e denote the equilibrium bond length and k the vibrational force constant.

1) (5 pts) Which molecular parameters are the same, to a very good approximation, for H_2 , D_2 , and HD ?

potential energy surface is same (k & R_e equal), but since masses are different, D₀, θ_v, & θ_r are different.

(a) none (b) k and R_e (c) k, R_e, and D₀ (d) k, R_e, D₀, θ_v, and θ_r

2) (5 pts) What are θ_r(HD) and θ_r(D₂) in K?

$\frac{\theta_r(HD)}{\theta_r(H_2)} = \frac{\mu(H_2)}{\mu(HD)} = \frac{3}{4}$, $\frac{\theta_r(D_2)}{\theta_r(H_2)} = \frac{\mu(H_2)}{\mu(D_2)} = \frac{1}{2}$

(a) 64.05, 42.70 (b) 85.4, 85.4 (c) 98.6, 120.8 (d) 113.9, 128.1

3) (5 pts) What are θ_v(HD) and θ_v(D₂) in K?

$\frac{\theta_v(HD)}{\theta_v(H_2)} = \sqrt{\frac{\mu(H_2)}{\mu(HD)}} = \sqrt{4/3} = 1.155$, $\frac{\theta_v(D_2)}{\theta_v(H_2)} = \sqrt{\frac{\mu(H_2)}{\mu(D_2)}} = \sqrt{1/2} = 0.707$

(a) 4650, 3105 (b) 5378, 4391 (c) 6210, 6210 (d) 7170, 8783

4) (5 pts) What is $((q(HD))^2 / (q(H_2) q(D_2)))_{trans}$ for the above reaction?

(a) 0.838 (b) 1.000 (c) 1.193 (d) 1.250 $\left(\frac{M_{HD}}{M_{H_2} M_{D_2}}\right)^{3/2} = \left(\frac{2}{2 \cdot 4}\right)^{3/2} = 1.193$

5) (5 pts) What is $2D_0(HD) - D_0(H_2) - D_0(D_2)$ in kJ/mole at 298.15 K?

(a) +464 (b) 4.37 (c) -0.644 (d) -4.37

6) (5 pts) Without doing a lengthy calculation, what is the approximate K_{eq} for the reaction at the top of the page around $T = 1000 \text{ K}$?

(a) 0.00 (b) 0.25 (c) 1.00 (d) 4.00

$$\sim \frac{\left(\frac{T}{\theta_r(HD)}\right)^2}{\left(\frac{T}{2\theta_r(H_2)}\right)\left(\frac{T}{2\theta_r(D_2)}\right)} \sim 4$$

$$D_0 = D_e - \frac{N_A h \nu}{2} = D_e - \frac{N_A k_B}{2} \left(\frac{h \nu}{k_B}\right) = D_e - \frac{1}{2} R \theta_v$$

$$2D_0(HD) - D_0(H_2) - D_0(D_2) = \frac{R}{2} (\theta_v(H_2) + \theta_v(D_2) - 2\theta_v(HD))$$

$$= \frac{.008314}{2} (6210 + 4391 - 10756) = -.644 \frac{\text{kJ}}{\text{mole}}$$

Chem 4120

First Problem Set

("Quantum Chemistry and Spectroscopy", by T. Engel, 2006)

Chapter 1) 1,2,3,4,6,7,8,9,10,11,12,13,15,17,19,20,21,22

Chem 4120

Second Problem Set

(“Quantum Chemistry and Spectroscopy”, by T. Engel, 2006)

Chapter 2) 4,5,6,7,8,9,10,11,12,14,15,16,17,18,21,22,23,29,30

Extra Problem

A water wave moves in the +x direction ~~at a speed of 1 m/s~~ and the distance between wave crests is 3 m. The crests of the wave have an amplitude of 0.2 m and it takes 5 seconds between wave crests to pass a fixed point in space. What are the wavelength, λ , and the frequency, ν , of the wave? Write down an expression for this traveling wave.

Chem 4120

Third Problem Set

(“Quantum Chemistry and Spectroscopy”, by T. Engel, 2006)

Chapter 4) 2,4,6,8,12,15,20,24

Chapter 5) 3,4

Extra Problems

- 1) A simple and approximate model of the electronic properties of linear conjugated models may be obtained by modeling the π electrons as a particle-in-a-box. Basically, the actual, but very complicated potential of the π electrons is replaced with a much simpler particle-in-a-box potential. The single (C-C) and double (C=C) bond lengths are .148 and .134 nm, respectively, and can be used to estimate the size of the box. Model the energy levels of 1,3,5 hexatriene and 1,3,5,7 octatetraene as particles in a box. As a consequence of the Pauli Exclusion Principle, only two electrons can occupy a single state. Identify which particle-in-a-box energy levels are filled for both of these molecules.
- 2) The lowest energy electronic transition frequently corresponds to an electron absorbing a photon and moving from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital). For the 1,3,5 hexatriene and 1,3,5,7 octatetraene particle-in-a-box models considered in the previous problem, estimate the wavelength of light, λ , necessary to promote an electron from the HOMO to LUMO level.
- 3) What happens to λ as the degree of conjugation increases? Can you give a simple physical explanation for why graphite is black?
- 4) Calculate the allowed energies and energy eigenfunctions for a particle constrained to move on a ring of radius R. The Hamiltonian (energy operator) is

$$H = -\frac{\hbar^2}{8\pi^2 m R^2} \frac{\partial^2}{\partial \theta^2}$$

where θ is an angular variable with a value between 0 and 2π and $\Psi(0) = \Psi(2\pi)$.

- 5) Use the particle-on-a-ring model to model benzene. Make a reasonable estimate of R and predict the wavelength of the lowest electronic transition of benzene.

Chem 4120

Fourth Problem Set

(“Quantum Chemistry and Spectroscopy”, by T. Engel, 2006)

Reading: Chapter 5, pages 61-68; Chapter 6, pages 81-92

Problems: 6-2, 6-4, and 6-7

Extra Problems

- 1) Derive an expression for $\sigma_x\sigma_p$ for a particle-in-a-box model for arbitrary n .
- 2) Model a solvated electron as a particle in a 1 dimensional box of side length a , and quantum number n . If the average energy equals $k_B T/2$ and $n = 5$, what must a be? (The idea here is that an electron will behave classically if n is fairly large and its average energy approaches the classical value expected from equipartition. This problem should give you a rough idea about the length scale required in order for an electron to behave like a billiard ball.)

Chem 4120

Fifth Problem Set

Vibration and Rotation

(“Quantum Chemistry and Spectroscopy”, by T. Engel, 2006)

Reading: Chapter 7: (entire); Chapter 8: Sections 8.1, 8.3, 8.4, 8.6, 8.9

Problems: Chapter 7: 1, 3, 7, 17, 19, 20
Chapter 8: 1, 3, 6, 14

Extra Problems

- 1) The solutions for the time independent Schrodinger equation for the rigid rotor are called spherical harmonics, $Y_L^m(\theta, \phi)$, and some examples are given on page 116 of Engel. Using these, show by direct integration that $Y_1^1(\theta, \phi)$ and $Y_2^0(\theta, \phi)$ are normalized and orthogonal. (The domain of integration for θ is from 0 to π and the domain of integration for ϕ is from 0 to 2π . Also, this involves a two dimensional integration where $dx dy \rightarrow \sin \theta d\theta d\phi$.)
- 2) Evaluate explicitly $\hat{l}_z Y_L^m(\theta, \phi)$ and $\hat{l}^2 Y_L^m(\theta, \phi)$ for $(L, m) = (1, 1)$ and $(2, 0)$. These are the same spherical harmonics considered in the previous problem. The angular momentum operators in spherical polar coordinates are

$$\hat{l}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$$\hat{l}^2 = -\hbar^2 \left[\frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta} \left(\sin(\theta) \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} \right]$$

Chemistry 4120/6120
6th Problem Set
Hydrogen, many electron atoms

Reading: Chapter 9 (entire), Chapter 10, Sections 10.1 through 10.6

Problems: Chapter 9: 1,2,3,4,6,7,8,9,12,15,16,19
Chapter 10: 2,3,4,8

Additional Problems:

- 1) Calculate the average kinetic, $\langle K \rangle$, and potential, $\langle V \rangle$, energies of an electron in the 1s orbital of hydrogen. The “virial theorem” in classical mechanics states that if the potential energy, $V(r)$, is a function only of distance, r , and $V(r) = k r^{n+1}$, (k and n are arbitrary constants), then $\langle K \rangle = (n+1)\langle V \rangle/2$. Is the “virial theorem” obeyed in quantum mechanics, (at least for hydrogen in its ground state)?
- 2) Determine whether the p_x and p_y orbitals are eigenfunctions of l_z . If not, does a linear combination exist that is an eigenfunction of l_z ?
- 3) The ‘size’ of an atom is sometimes considered to be measured by the radius of a sphere that contains 90% of the charge density of the electrons in the outermost occupied orbital. Calculate the ‘size’ of a hydrogen atom in its ground state according to this definition.
- 4) Is an electron further from the nucleus, on average, when it is in a 2s or 2p orbital?
- 5) According to the Aufbau principle, estimate the ground state electronic configurations of: O, Sc, Cu, Zn, Eu, Bk, and the (undiscovered) superheavy element with atomic number 126. (Glenn Seaborg, who is credited with the discovery of a number of the transuranium elements, believed that elements with atomic number around 126 should be stable, but none has ever been found in nature or “synthesized” in a cyclotron or supercollider.)

Chemistry 4120/6120

7th Problem Set

Term Symbols, Introduction to Chemical Bonding

Reading: Chap. 10 (Section 10-7), Chap. 12 (entire), Chap. 13 (Sections 13-1 through 13-7)

Problems: Chapter 10: 18
Chapter 12: 2,4
Chapter 13: 5,6,7,8,9,10,11,12

Chemistry 4120/6120

8th Problem Set

Introduction to Statistical Thermodynamics

(Note that we are now using the “green” book: “Thermodynamics, Statistical Thermodynamics, and Kinetics,” by Thomas Engel & Philip Reid)

Reading: Chap. 12 (Sections 12.1, 12.2, 12.3), Chap. 13 (Sections 13.1, 13.2.1, 13.4), Chap. 14 (entire)

Problems: Chapter 12: 1,3,7,9,11,14
Chapter 13: 7,9,10,11,14,16,20
Chapter 14: 2,5,6,8,14,18,24,26

Chemistry 4120/6120

9th Problem Set

Statistical Thermodynamics – Chemical Equilibrium

(Note that we are now using the “green” book: “Thermodynamics, Statistical Thermodynamics, and Kinetics,” by Thomas Engel & Philip Reid)

Reading: Chap. 15 (entire)

Problems: Chapter 15: 4, 5, 6, 15, 24, 31

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial \phi}$$

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right]$$

Solutions For Rigid Rotor

$$\hat{H} \psi = E \psi$$

$$\frac{1}{2I} \hat{L}^2 \psi(\theta, \phi) = E \psi(\theta, \phi)$$



depends on θ & ϕ

In this course, we won't derive the solutions, but only write them down. Like the 2 dimensional particle in a box, we expect 2 quantum numbers.

The energy eigen functions are:
 spherical harmonics $Y_{\ell, m}(\theta, \phi) = \Theta_{\ell, m}(\theta) \Phi_m(\phi)$
 see p. 116 depend only on θ $\frac{1}{\sqrt{2\pi}} e^{im\phi}$

$$\frac{1}{2I} \hat{L}^2 Y_{\ell, m} = E_{\ell} Y_{\ell, m}$$

$$E_{\ell} = \ell(\ell+1) \hbar^2 / 2I$$

$$L_{\ell}^2 = \hbar^2 \ell(\ell+1)$$

$$\ell = 0, 1, 2, 3, \dots$$

$$m = 0, \pm 1, \pm 2, \dots, \pm \ell$$

Note: $Y_{J,m}$ are eigenfunctions of \hat{L}^2 and \hat{L}_z . What does this mean?

Allowed states:

$$\text{IF } J=0, \quad m=0 \quad (1 \text{ state})$$

$$E_0 = 0$$

$$\text{IF } J=1, \quad m=0, \pm 1 \quad (3 \text{ states})$$

$$E_1 = 2\hbar^2/2I$$

$$\text{IF } J=2, \quad m=0, \pm 1, \pm 2 \quad (5 \text{ states})$$

$$E_2 = (2)(3)\hbar^2/2I$$

etc.

Physical Significance of m

Consider $\hat{L}_z Y_{J,m} = -i\hbar \frac{\partial}{\partial \phi} \left[Y_{J,m}(\theta) \frac{1}{\sqrt{2\pi}} e^{im\phi} \right]$

$$= \frac{-i\hbar}{\sqrt{2\pi}} Y_{J,m}(\theta) \frac{\partial}{\partial \phi} e^{im\phi} = m\hbar \left[Y_{J,m}(\theta) \frac{1}{\sqrt{2\pi}} e^{im\phi} \right]$$

$\underbrace{\qquad\qquad\qquad}_{ime^{im\phi}}$

$$\hat{L}_z Y_{J,m} = m\hbar Y_{J,m}$$

\therefore the $Y_{J,m}$ are also eigenfunctions of \hat{L}_z with eigenvalues $m\hbar$.

$\therefore m$ — related to component of a.m.

$$C_V = \left(\frac{\partial U}{\partial T} \right)_{N,V} = \frac{\partial}{\partial T} \left(-ND_0 + \frac{5}{2}RT \right) = \frac{5}{2}R$$

$$\approx 20.79 \frac{\text{J}}{\text{mole K}}$$

$$C_P = C_V + R = 29.10 \text{ J/mole K} \quad \leftarrow \text{(valid for ideal gas)}$$

How does this compare to experiment?

Consider 298°K

gas	C_p (J/mole K)
H_2	28.84
HF	29.14
HCl	29.14
HBr	29.13
N_2	29.13
O_2	29.38
Cl_2	33.95
I_2	36.9

(a) discrepancy due to inaccurate accounting of q_{rot}

(b) due to q_{vib} ($\theta_v(Cl_2) = 810 \text{ K}$, $\theta_v(I_2) = 310 \text{ K}$)

Consider q_{vib} when $\theta_v \ll T$

$$q_{vib} = \frac{\sum_{i=1}^{\infty} e^{-\beta \epsilon_i}}{(1 - e^{-\theta_v/T})} \approx \frac{T}{\theta_v} \sum_{i=1}^{\infty} e^{-\beta \epsilon_i}$$

$$\ln Q = N \ln [q_{vib} q_{rot} q_{trans}] - \ln N!$$

$$= N \ln \sum_{i=1}^{\infty} e^{-\beta \epsilon_i} + \beta N D_0 + N \ln \left(\frac{T}{\theta_v} \right) + N \ln \left(\frac{T}{\theta_r} \right) + N \ln \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}$$

$$+ \frac{3}{2} N \ln T - \ln N!$$

$$U = k_B T^2 \left(\frac{\partial \ln Q}{\partial T} \right)_{N,V} = k_B T^2 \left[\frac{\partial}{\partial T} \left(\frac{N D_0}{R_0 T} + N \ln T + N \ln T + \frac{3}{2} N \ln T + \text{const.} \right) \right]$$

$$= -N/D_0 + \frac{7}{2} R T$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \frac{\partial}{\partial T} (-ND_1 + \overset{\approx 0}{\frac{7}{2}} RT) = \frac{7}{2} R$$

$$C_P \approx C_V + R = \frac{9}{2} R = 37.41 \frac{\text{J}}{\text{mole K}}$$

This is higher than all the gases considered, but I_2 approaches it.

$$h = 6.626 \times 10^{-34} \text{ J/sec}, \quad k_B = 1.38 \times 10^{-23} \frac{\text{J}}{\text{K}}$$

$$n = \frac{2a}{h} \sqrt{m k_B T}$$

System	m (kg)	a (m)	n	comment
He-atom in 1 cm box, 25°C	6.64×10^{-27}	10^{-2}	1.58×10^8	behaves classically
He-atom in 2 \AA box, 25°C	"	2×10^{-10}	3.16	(borderline)
He-atom in 2 \AA box, 4°K	"	"	.366	need q.m.
electron in 2 \AA box at 25°C	9.11×10^{-31}	"	.037	need q.m.

Conclusions:

1) atoms in macroscopic boxes ($a \gtrsim 10 \text{ \AA}$) well explained by classical mechanics.

2) atoms in small boxes (atoms in liquid "cages") might be adequately treated by classical mechanics at room temperature, but not low T (example of helium at low T)

\Rightarrow 3) electrons in atoms - need quantum mechanics!

acy is attained. The behavior of $\bar{C}_{v(\text{rot})}/R$ as a function of temperature is shown in 29.1. It is clear from the figure that at all values of $T/\theta_r > \sim 1.2$, the heat capacity has reached the classical value, R . Suppose that we estimate the value of θ_r for a molecule such as O_2 . Since $m = (0.028 \text{ kg/mol})/(6 \times 10^{23}/\text{mol}) \approx 5 \times 10^{-26} \text{ kg}$, then $I = mr^2 \approx (5 \times 10^{-26} \text{ kg})(10^{-10} \text{ m})^2 \approx 5 \times 10^{-46} \text{ kg m}^2$, and

$$\theta_r = \frac{(1 \times 10^{-34} \text{ J s})^2}{2(5 \times 10^{-46} \text{ kg m}^2)(1 \times 10^{-23} \text{ J/K})} \approx 1 \text{ K.}$$

The actual values of θ_r , as well as θ_v , are given in Table 29.1. Except for those diatomic molecules containing hydrogen, the values of θ_r are indeed about 1 to 2 K. Thus these molecules have the classical value of the heat capacity at any temperature above about

When $\theta_r/T \ll 1$, we can replace the sum in Eq. (29.55) by an integral. Let $y = J(J + 1)$; $dy = (2J + 1) dJ$. But since J is an integer, the difference between successive values is just $dJ = 1$ and therefore $dy = 2J + 1$. Using this result in Eq. (29.55) and replacing summation by integration, we obtain

$$q_r = \int_0^\infty e^{-y\theta_r/T} dy = \frac{T}{\theta_r} = \frac{2IkT}{h^2} \quad (29.59)$$

Table 29.1
Parameters for diatomic molecules

	θ_v/K	θ_r/K	r_e/pm	$D_0/10^{-19} \text{ J}$
H_2	6210	85.4	74.0	7.174
N_2	3340	2.86	109.5	15.637
O_2	2230	2.07	120.4	8.196
CO	3070	2.77	112.8	17.798
NO	2690	2.42	115.0	10.426
HCl	4140	15.2	127.5	7.109
HBr	3700	12.1	141.4	5.071
HI	3200	9.0	160.4	4.892
Cl_2	810	0.346	198.9	3.985
Br_2	470	0.116	228.4	3.158
I_2	310	0.054	266.7	2.474

From T. L. Hill, *Introduction to Statistical Thermodynamics*. Reading, Mass.: Addison-Wesley, 1960.