CHM2330 Midterm Tuesday, March. 6th, 2012

Name: ______________________________

Student #: ______________________________

This is a closed book exam with no notes allowed. Calculators are permitted.
Write all the formulas that you use to solve the questions and show all your work.
Be sure to include units and the correct number of significant digits in your answer.

Constants and Data:

$R = 8.314$ J K^{-1} mol^{-1} = N_A*k

k=1.381 x 10^{-23} J K^{-1}

N_A = 6.023 x 10^{23} mol^{-1}

h = 6.6261 x 10^{-34} J s

c = 2.9979 x 10^{8} m s^{-1}

1 m = 100 cm = 10^{9} nm

1 W = 1 J s^{-1}

1 J = 1 kg m^{2} s^{-2}

1 Pa = 1 kg m^{-1} s^{-1}

1 mol dm^{-3} = 1 M = 1000 mM

1 atm = 760 Torr = 101325 Pa = 1.01325 bar

Formula sheet is on last page - this can be removed and does not have to be handed in.

Q1: __________/9 Q2: __________/7 Q3: __________/5 Q4: __________/9 Q5: __________/4

Q6: __________/11

Total = __________/45

Question 1

All of the statements shown below are FALSE. **For 3 out of 4** of these statements (9 marks):

i. Explain why the original statement is false in ~1 - 2 sentences.
ii. Change the statement to make it correct.

a) If reactant A is in equilibrium with its product P, then the rate ~~constant~~ of the forward reaction will equal the rate ~~constant~~ of the reverse reaction.

Rate constants are a characteristic of a reaction that are constant – they do not change with reagent concentration. Therefore the rate constant at equilibrium is the same as the rate constant at any other point in the reaction. It is the reaction rates that change with reagent concentrations.

b) Suppose a reaction occurs according to the following kinetic reaction mechanism:

$$A \xrightarrow{k_a} I \xrightarrow{k_b} P$$

If the ~~second~~ first elementary reaction is very slow compared to the ~~first~~ second elementary reaction, then it is possible to use the steady state approximation to derive the integrated rate equation.

If the second elementary reaction is slow then there will be a rapid accumulation of the intermediate until the reagent A is depleted. Then the concentration of intermediate will decrease slowly as it is converted into product. The concentration of intermediate will never be constant and hence no steady state condition will be achieved.

c) When the concentration of product generated in an enzyme-catalyzed reaction is graphed as a function of time, a plateau in the graph will occur when the reaction reaches ~~steady-state conditions~~.

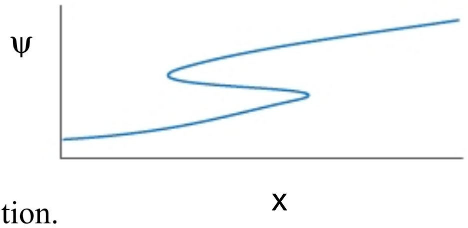
The product concentration will increase over time until all the substrate is depleted. At this point the graph will level out into a plateau. The system is at steady-state before this plateau is reached.

d) According to quantum mechanics, the trajectory of an object undergoing free translational motion ~~will not be linear, but will follow the trajectory of a wave with $\lambda = h/p$~~ can not be known for microscopic objects.

In quantum mechanics, a particle is distributed through space like a wave, with a wavelength that is defined by the deBroglie wavelength. We can no longer talk about a defined trajectory, we instead must talk about a wavefunction, ψ that describes the wavelike properties of a particle.

Question 2
Provide a short answer for **7 out of the 8** questions below. In some cases the answer can be provided either as a symbol from the equation sheet, or described in words. No explanations for your answers are required, as only the answer will be marked.

a) According to the Born Interpretation, the function shown on the right can not be a solution to the Schrodinger equation because:



There is more than one value for some positions in the wavefunction. A single probability at these positions can not be calculated, hence this is not a physically reasonable wavefunction.

b) The area under an energy distribution curve corresponds to what property of a black body?

Energy density

c) What is the elementary reaction that has k_{cat} as its rate constant in the Michaelis-Menten mechanism?

$$\mathrm{ES} \xrightarrow{k_{cat}} \mathrm{E} + \mathrm{P}$$

d) According to the kinetic theory of gases, does the distribution of molecular speeds increase, decrease, or remain unchanged as the temperature of the gas is increased?

The distribution of speeds increases.

e) Is the Michaelis-Menten equation an empirical rate equation or an integrated rate equation?

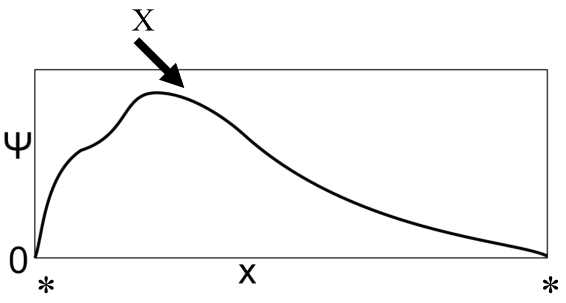
Emprical

f) According to the Lindenmann-Hinshelwood mechanism for gas-phase isomerization, the order of the reaction at low pressures will be:

2^{nd} order at low pressures

g) For the graph of ψ shown below label the node(s) with an *.

h) For ψ shown below label the place you are most likely to find the particle with an X.



Question 3
Write down the equation from the formula sheet (exactly as it is given) that best describes **5 of the 6** scenarios below: (5 marks)

a) Ultraviolet catastrophe $\rho = \dfrac{8\pi kT}{\lambda^4}$

b) Graham's Law of Effusion $Z_W = \dfrac{P}{\sqrt{2\pi mkT}}$

c) The Schrodinger Equation $-\dfrac{\hbar^2}{2m}\dfrac{d^2\psi}{dx^2} + V(x)\psi = E\psi$

d) The wave-like property of particles $\lambda = \dfrac{h}{p}$

e) The kinetic energy of a photoelectron $h\nu = \dfrac{1}{2}mv^2 + \Phi$

f) The mean speed of molecules in an ideal gas $\bar{c} = \sqrt{\dfrac{8RT}{\pi M}}$

Question 4
Suppose the reaction $3A \rightarrow A_3$ is second order with respect to A.

a) Is it possible to conclude that the overall reaction is comprised of more than one elementary reaction? Provide a short explanation for your answer. (2 marks)

Yes, it must be comprised of more than one elementary reaction. (If it is 2nd order with respect to reagent A then the rate determining step must have the form $\mathrm{A + A \longrightarrow I}$ where I is an intermediate. One molar equivalent of A must still react to form the final produt A_3 – hence at least one more elementary reaction will be required.

b) If the rate of this reaction is given in units of mol dm^{-3} min^{-1} then what are the units of the rate constant? (1 mark)

$$v = k[\mathrm{A}]^2$$

$$\text{mol dm}^{-3}\ \text{min}^{-1} = k\left(\text{mol dm}^{-3}\right)^2$$

$$\text{unit of } k = \frac{\left(\text{mol dm}^{-3}\ \text{min}^{-1}\right)}{\left(\text{mol dm}^{-3}\right)^2} = \text{mol}^{-1}\ \text{dm}^{3}\ \text{min}^{-1}$$

c) Derive the integrated rate law for this reaction. (4 marks)

$$v = -\frac{1}{3}\frac{d[\mathrm{A}]}{dt} \quad \text{(1 mark)}$$

$$v = k[\mathrm{A}]^2 \quad \text{(1 mark)}$$

$$-\frac{1}{3}\int_{[\mathrm{A}]_o}^{[\mathrm{A}]} \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = \int_0^t k\,dt \quad \text{(1 mark)}$$

$$-\frac{1}{3}\left|\frac{1}{[\mathrm{A}]}\right|_{[\mathrm{A}]_o}^{[\mathrm{A}]} = kt$$

$$-\frac{1}{3}\frac{1}{[\mathrm{A}]} + \frac{1}{[\mathrm{A}]_o} = kt \quad \text{(1 mark)}$$

d) Will $\Delta S^{\ddagger}$ be greater than, less than or equal to zero for the rate-determining step? Provide a one-sentence justification of your answer. (2 marks)

$\Delta S^{\ddagger}$ will be less than zero (1 mark)

The difference in entropy between the reactants and the transition state will be negative because two species that are able to undergo free translation and rotation come together to form just one species that would translate and rotate together. The loss in the number of degrees of freedom when forming the transition state decreases the entropy, making $\Delta S^{\ddagger}$ negative. (1 mark)

Question 5

Use the Maxwell distribution of speeds to estimate the fraction of H_2 molecules (M_{H_2}=2.0016 g/mol) that have speeds in the range of 990 m s^{-1} to 1000 m s^{-1} at 310 K. (4 marks)

Since we are finding the probability over a narrow range of speeds, we can calculate the average Maxwell distribution for this range $f(v_{\text{avg}})$ and multiply this by the interval Δv.

$$f(v_{avg}) = 4\pi\left(\frac{M}{2\pi RT}\right)^{\frac{3}{2}} v_{avg}^2 \exp\left(-\frac{Mv_{avg}^2}{2RT}\right) \quad \text{(1 mark) where } v_{\text{avg}} = 995 \text{ m/s}$$

$$f(v_{avg}) = 4\pi\left(\frac{2.0016\ \text{g mol}^{-1}\left(10^{-3}\ \text{kg g}^{-1}\right)}{2\pi\left(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\right)\left(310\ \text{K}\right)}\right)^{\frac{3}{2}}\left(995\ \text{m s}^{-1}\right)^2 \exp\left(-\frac{\left(2.0016\ \text{g mol}^{-1}\right)\left(10^{-3}\ \text{kg g}^{-1}\right)\left(995\ \text{m s}^{-1}\right)^2}{2\left(8.314\ \text{J K}^{-1}\ \text{mol}^{-1}\right)\left(310\ \text{K}\right)}\right)$$

$$f(v_{avg}) = 3.7\times10^{-4}\ \text{s m}^{-1} \quad \text{(1 mark)}$$

Fraction of molecules with speeds between 990 m s^{-1} to 1000 m s^{-1}:

$$f(v_{avg})\Delta v = \left(3.7\times10^{-4}\ \text{s m}^{-1}\right)\left(10\ \text{m s}^{-1}\right) = 3.7\times10^{-3} \quad \text{(1 mark)}$$

or 0.37% of the population. (1 mark)

Question 6

The ground state wavefunction for a particle confined to a one-dimensional box of length L is

$$\psi = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right)$$

a) Show that this wavefunction is or is not an eigenfunction of the linear momentum operator. (3 marks)

$$\hat{p}_x\psi = \frac{\hbar}{i}\sqrt{\frac{2}{L}}\frac{d\left(\sin\left(\frac{\pi x}{L}\right)\right)}{dx}$$ (1 mark)

$$\hat{p}_x\psi = \frac{\hbar}{i}\sqrt{\frac{2}{L}}\frac{-L}{\pi}\cos\left(\frac{\pi x}{L}\right)$$ (1 mark)

Since we do not get the same wavefunction after doing the operation, this is not an eigenfunction of the linear momentum operator. (1 mark)

b) Show that this wavefunction is or is not normalized. (4 marks)

$$\int_0^L \psi^* \psi \, dx$$ (1 mark)

$$= \frac{2}{L}\int_0^L \sin^2\left(\frac{\pi x}{L}\right)dx$$ (1 mark)

$$= \frac{2}{L}\left|\frac{x}{2} - \frac{\sin 2\left(\frac{\pi}{L}\right)x}{4\left(\frac{\pi}{L}\right)}\right|_0^L = 1$$ (1 mark)

Therefore the wavefunction is normalized. (1 mark)

c) What are the possible values that you could obtain if you were to measure the linear momentum of this particle? You must show your work for full marks. (4 marks)

Since this wavefunction is not an eigenfunction of the linear momentum operator we must express it as a superposition of wavefunctions that are eigenfunctions of this operator using:

$$\cos x = \frac{1}{2}\left(e^{ix} + e^{-ix}\right)$$

$$\psi = \sqrt{\frac{2}{L}}\sin\left(\frac{\pi x}{L}\right) = \sqrt{\frac{2}{L}}\frac{1}{2i}\left(e^{\frac{i\pi x}{L}} - e^{\frac{-i\pi x}{L}}\right) = \sqrt{\frac{2}{L}}\frac{1}{2i}e^{\frac{i\pi x}{L}} - \sqrt{\frac{2}{L}}\frac{1}{2i}e^{\frac{-i\pi x}{L}} = \psi_+ + \psi_-$$ (1 mark)

$$\hat{p}_x\psi = \frac{\hbar}{i}\sqrt{\frac{2}{L}}\frac{1}{2i}\frac{d\left(e^{\frac{i\pi x}{L}} - e^{\frac{-i\pi x}{L}}\right)}{dx}$$ (1 mark)

$$\hat{p}_x\psi = \frac{\hbar}{i}\sqrt{\frac{2}{L}}\frac{1}{2i}\left(\frac{i\pi}{L}e^{\frac{i\pi x}{L}} - \frac{-i\pi}{L}e^{\frac{-i\pi x}{L}}\right)$$ (1 mark)

$$\hat{p}_x\psi = \frac{\hbar}{i}\frac{i\pi}{L}\sqrt{\frac{2}{L}}\frac{1}{2i}e^{\frac{i\pi x}{L}} + \frac{\hbar}{i}\frac{-i\pi}{L}\left(-\sqrt{\frac{2}{L}}\frac{1}{2i}e^{\frac{-i\pi x}{L}}\right) = \frac{\hbar\pi}{L}\psi_+ + \frac{-\hbar\pi}{L}\psi_-$$

Therefore there will be two possible values for linear momentum $\frac{\hbar\pi}{L}$ and $-\frac{\hbar\pi}{L}$. (1 mark)

CHM2330 Midterm Formula Sheet

This page can be removed from the midterm.

$$E_k = \tfrac{1}{2}mv^2 \qquad f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 \exp\left(-Mv^2/2RT\right)$$

$$c = \sqrt{\frac{3RT}{M}} \qquad \bar{c} = \sqrt{\frac{8RT}{\pi M}} \qquad c^* = \sqrt{\frac{2RT}{M}} \qquad \bar{c}_{rel} = \sqrt{\frac{8kT}{\pi\mu}}$$

$$\mu = \frac{m_A m_B}{m_A + m_B} \qquad z = \frac{\sigma \bar{c}_{rel} P}{kT} \qquad \lambda = \frac{kT}{\sqrt{2}\sigma P} \qquad Z_W = \frac{P}{\sqrt{2\pi mkT}}$$

$$\upsilon = \frac{1}{v_X}\frac{d[\mathrm{X}]}{dt} \qquad K = \frac{k_a}{k_a'}\frac{k_b}{k_b'}\frac{k_c}{k_c'}\cdots \qquad k = Ae^{-\frac{Ea}{RT}} \qquad \upsilon_o = \frac{k_{cat}[\mathrm{E}]_o[\mathrm{S}]_o}{K_M + [\mathrm{S}]_o}$$

$$E_a = RT^2\left(\frac{d\ln k}{dT}\right) \qquad k_2 = P\sigma\sqrt{\frac{8kT}{\pi\mu}}N_A e^{-E_a/RT} \qquad \frac{1}{k} = \frac{k_a'}{k_a k_b} + \frac{1}{k_a[A]}$$

$$k_r = \left(\frac{kT}{h}\right)\left(\frac{RT}{p^o}\right)\exp\left(\frac{\Delta S^\ddagger}{R}\right)\exp\left(\frac{-\Delta H^\ddagger}{RT}\right) \qquad E_a = \Delta H^\ddagger + RT$$

$$T\lambda_{\max} = \frac{1}{5}c_2 \qquad \mathrm{M} = \sigma T^4 \qquad d\mathcal{E} = \rho\, d\lambda \qquad \rho = \frac{8\pi kT}{\lambda^4}$$

$$E = nh\nu \qquad \nu = \frac{c}{\lambda} \qquad \rho = \frac{8\pi hc}{\lambda^5\left(e^{hc/\lambda kT} - 1\right)} \qquad h\nu = \frac{1}{2}mv^2 + \Phi$$

$$\lambda = \frac{h}{p} \qquad -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + V(x)\psi = E\psi \qquad P = \int|\psi|^2\, d\tau \qquad N^2\int \psi^*\psi\, dx = 1$$

$$dx\, dy\, dz = r^2\, dr\, \sin\theta d\theta d\phi \qquad \hat{x} = x\times \qquad \hat{p}_x = \frac{\hbar}{i}\frac{d}{dx} \qquad \psi = \sum_k c_k\psi_k$$

$$\frac{d\sin u}{dx} = \cos u\frac{du}{dx} \qquad \frac{d\cos u}{dx} = -\sin u\frac{du}{dx}$$

$$\int \sin^2 ax\, dx = \frac{x}{2} - \frac{\sin 2ax}{4a} + C \qquad \int \sin ax\, dx = -\frac{1}{a}\cos ax + C \qquad \int \cos ax\, dx = \frac{1}{a}\sin ax + C$$

$$e^{ix} = \cos x + i\sin x \qquad \cos x = \frac{1}{2}\left(e^{ix} + e^{-ix}\right) \qquad \sin x = \frac{1}{2i}\left(e^{ix} - e^{-ix}\right)$$