1. (10 points) The diffusion coefficient of lysozyme (MW = 14.1 kg/mol is $0.104 \times 10^{-9} \text{m}^2\text{s}^{-1}$). How long does it take this protein, on average, to diffuse an rms distance of exactly 1 µm in solution?

The root-mean-square distance traveled in three-dimensional diffusion is

$$\sqrt{\langle r^2 \rangle} = \sqrt{6Dt}$$

Substitution into this equation gives the result:

$$t = \frac{\langle r^2 \rangle}{6D} = \frac{(1 \times 10^{-6} \text{m})^2}{6 \times 0.104 \times 10^{-9} \text{m}^2\text{s}^{-1}} = 1.60 \times 10^{-3} \text{s} = 1.6 \text{ms}$$
2. (10 points) Iodine reacts with a ketone in aqueous solution to form an iodoketone by the following reaction:

$$I_2 + \text{ketone} \rightarrow \text{iodoketone} + I^- + H^+$$

Birk and Walters (J. Chem. Ed., 69, 585 – 587 (1992)) report the following initial-rate data for the iodination of acetone measured at 23°C.

<table>
<thead>
<tr>
<th>[Acetone] (mol dm⁻³)</th>
<th>[H⁺] (mol dm⁻³)</th>
<th>[I₂] (mol dm⁻³)</th>
<th>10⁶ × Initial rate (mol dm⁻³ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.33</td>
<td>0.0404</td>
<td>0.00665</td>
<td>1.85</td>
</tr>
<tr>
<td>1.33</td>
<td>0.0809</td>
<td>0.00665</td>
<td>3.89</td>
</tr>
<tr>
<td>0.333</td>
<td>0.323</td>
<td>0.00665</td>
<td>3.76</td>
</tr>
<tr>
<td>0.667</td>
<td>0.323</td>
<td>0.00665</td>
<td>7.55</td>
</tr>
<tr>
<td>0.333</td>
<td>0.323</td>
<td>0.00332</td>
<td>3.75</td>
</tr>
</tbody>
</table>

Write the rate law for this reaction, showing the orders with respect to the reactants and the hydrogen ion. Show your work and explain how you got the answers.

[HINT: Remember that orders are generally whole numbers (or perhaps half order). So, a slight difference from integral orders may be considered to be due to experimental error.]

The various orders are found by taking the appropriate ratios. For example, since the iodine and acetone are constant in the first two experiments, it can be used to determine the dependence on hydrogen ion concentration:

$$\left( \frac{0.404}{0.0809} \right)^n = \frac{1.85}{3.89}$$

Taking the logarithm of both sides gives the following equation:

$$-0.69438n = -0.74322$$

Solving this for $n$ gives:

$$n = \frac{0.74322}{0.69438} = 1.07$$, which is close to 1.

Similarly one may use the third and fourth experiments to determine the order with respect to acetone.

$$\left( \frac{0.333}{0.667} \right)^n = \frac{3.76}{7.55}$$

Taking the logarithm of both sides gives the following equation:

$$-0.69465n = -0.6971$$

Solving this for $n$ gives:

$$n = \frac{0.6971}{0.69465} = 1.00$$.

Finally, one may use the third and fifth experiments to determine the order with respect to iodine:

$$\left( \frac{0.00665}{0.00332} \right)^n = \frac{3.76}{3.75}$$

Taking the logarithm of both sides gives the following equation:

$$0.69465n = 0.00266$$

Solving this for $n$ gives:

$$n = \frac{0.00266}{0.69465} = 0.004$$, which is close to 0.

So, the rate equation looks like this:

$$v = k[Aacetone]^1[H^+]^1[I_2]^0 = k[Aacetone][H^+]$$

Interestingly, it does not depend on the concentration of iodine.
3. (10 points) Viscosity, like many other dynamic processes, can be considered to be thermally activated. If that is the case, the viscosity obeys the equation: \( \eta(T) = \eta_0 e^{E/RT} \), where \( \eta_0 \) is a pre-exponential factor and \( E \) is an activation energy. The viscosity of liquid benzene has been measured over a relatively wide range of temperature, as given in the table. From these data, determine the values of \( \eta_0 \) and \( E \) for benzene. Show your work clearly. [HINT: Be careful. Note that the formula is subtly different from the Arrhenius formula for the temperature dependence of a rate constant.]

<table>
<thead>
<tr>
<th>( T (\degree C) )</th>
<th>( \eta ) (cP)</th>
<th>T(K)</th>
<th>( 1/T ) (1/K)</th>
<th>ln(( \eta/cP ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.836</td>
<td>278.15</td>
<td>0.00359</td>
<td>-0.179127</td>
</tr>
<tr>
<td>40</td>
<td>0.492</td>
<td>313.15</td>
<td>0.00319</td>
<td>-0.709277</td>
</tr>
<tr>
<td>80</td>
<td>0.318</td>
<td>353.15</td>
<td>0.00283</td>
<td>-1.145704</td>
</tr>
<tr>
<td>120</td>
<td>0.219</td>
<td>393.15</td>
<td>0.00254</td>
<td>-1.518684</td>
</tr>
<tr>
<td>160</td>
<td>0.156</td>
<td>433.15</td>
<td>0.00230</td>
<td>-1.857899</td>
</tr>
</tbody>
</table>

The plot of the logarithm of the viscosity versus \( 1/T \) should be linear. The intercept is logarithm of \( \eta_0 \), and \( E \) can be determined from the slope.

Using the data on the plot, one finds that \( \eta_0 = \exp(-4.8176) \text{ cP} = 0.008086 \text{ cP} \)

The activation energy is: \( E = \text{slope} \times R = (1290.5 \text{ K})(8.3144349 \text{ J K}^{-1} \text{ mol}^{-1}) = 10.73 \text{ kJ mol}^{-1} \)
4. **(10 points)** For each of the phrases in column A, match it with the appropriate statement or definition in column B, by putting the proper number in the blank.

<table>
<thead>
<tr>
<th>Column A</th>
<th>Column B</th>
</tr>
</thead>
<tbody>
<tr>
<td>14 Activated complex theory</td>
<td>1. Approximation that the concentrations of reactive intermediates do not change in time.</td>
</tr>
<tr>
<td>15 Electrophoresis</td>
<td>2. Chemical process that occurs in a single step</td>
</tr>
<tr>
<td>2 Elementary step</td>
<td>3. Constant in the Arrhenius equation</td>
</tr>
<tr>
<td>10 Initial rate method</td>
<td>4. Correction for the friction coefficient of nonspherical molecules</td>
</tr>
<tr>
<td>8 Laminar flow</td>
<td>5. Describes how the reaction rate depends on concentration</td>
</tr>
<tr>
<td>4 Perrin factor</td>
<td>6. Diffusion limits the reaction rate</td>
</tr>
<tr>
<td>12 Random walk</td>
<td>7. Equation for the rms velocity</td>
</tr>
<tr>
<td>5 Reaction order</td>
<td>8. Flow may be decomposed into layers of constant speed</td>
</tr>
<tr>
<td>13 Sedimentation coefficient</td>
<td>9. Graph of potential energy of configurations</td>
</tr>
<tr>
<td>1 Steady-state approximation</td>
<td>10. Measurement of change at the earliest times of a reaction</td>
</tr>
<tr>
<td></td>
<td>11. Moving through a gel in a worm-like fashion</td>
</tr>
<tr>
<td></td>
<td>12. Series of steps, each of which is not correlated with the previous or subsequent step in direction</td>
</tr>
<tr>
<td></td>
<td>13. Terminal velocity divided by the acceleration</td>
</tr>
<tr>
<td></td>
<td>14. Transition state theory</td>
</tr>
<tr>
<td></td>
<td>15. Transport that occurs when a charged molecule is placed in an electric field</td>
</tr>
</tbody>
</table>
5. (10 points) In the stratosphere, ozone is converted to molecular oxygen by reaction with atomic chlorine:

\[ \text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2 \]

The rate constant for this second-order reaction is thermally activated and is

\[ k = \left(1.7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}\right) e^{-260 K / T}, \]

where the temperature is in kelvins. At 20 km above the surface of the Earth, the temperature may be assumed to be –50°C. (a) What is the rate constant, \( k \), for this reaction 20 km above the surface of the Earth?

First, calculate the temperature in kelvins.

\[ T = (273.15 – 50)K = 223.15 \text{ K} \]

Use the equation to calculate the rate constant:

\[ k = \left(1.7 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1}\right) \exp\left(- \frac{260 K}{223.15 K}\right) = 5.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1} \]

(b) At 20 km above the Earth’s surface, the concentration of ozone is roughly \( 8 \times 10^{-11} \text{ mol dm}^{-3} \). Assuming a small concentration of chlorine atoms (say \( 5 \times 10^{-17} \text{ mol dm}^{-3} \)) at 20 km above the surface of the Earth, what is the rate of the reaction [i.e. \( -\frac{d[O_3]}{dt} \)] under these conditions?

This is a simple plug in problem.

\[ v = k[O_3][Cl] = (5.3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{s}^{-1})(8 \times 10^{-11} \text{ mol dm}^{-3})(5 \times 10^{-17} \text{ mol dm}^{-3}) \]

\[ = 2.12 \times 10^{-17} \text{ mol dm}^{-3} \text{s}^{-1} \]
6. (10 points) The thermal decomposition of ozone to form oxygen by the reaction

\[ 2O_3 \rightarrow 3O_2 \]

is very complex. Here is a simplified mechanism for this reaction:

\[
\begin{align*}
O_3 & \rightarrow k_1 O_2 + O \\
O_2 + O & \rightarrow k_2 O_3 \\
O + O_3 & \rightarrow k_3 2O_2
\end{align*}
\]

(a) What is the reactive intermediate in this reaction?

The reactive intermediate is the oxygen atom.

(b) Give two expressions for the rate of reaction, one in terms of the time derivative of the ozone concentration and one in terms of the time derivative of the oxygen concentration.

\[
v = -\frac{1}{2} \frac{d[O_3]}{dt} = \frac{1}{3} \frac{d[O_2]}{dt}
\]

(c) Using the appropriate steady-state approximation, derive an expression for the rate of reaction in terms of oxygen and ozone concentrations.

The reaction rate, expressed in terms of the production of oxygen is:

\[
v = \frac{1}{3} \frac{d[O_2]}{dt} = \frac{1}{3} (v_1 - v_2 + 2v_3)
\]

Using the steady-state approximation on the oxygen atom gives the equation:

\[
\frac{d[O]}{dt} = 0 = v_1 - v_2 - v_3 \quad \Rightarrow \quad v_1 - v_2 = v_3
\]

Using this result in the above equation gives

\[
v = v_3
\]

Using the steady state approximation, one also has

\[
k_1[O_3] = k_2[O_2][O] + k_3[O_3][O] \quad \Rightarrow \quad [O] = \frac{k_1[O_3]}{k_2[O_2] + k_3[O_3]}
\]

Then substitution of this value gives the steady-state rate law:

\[
v = v_3 = k_3[O_3][O] = k_1k_3 \frac{[O_3]^2}{k_2[O_2] + k_3[O_3]}
\]
7. (10 points) Protein tyrosine phosphatases (PTPases) are enzymes that control tyrosine phosphorylation, a process involved in the regulatory functions in a cell. Sarmieto et al. [Journal of Medicinal Chemistry, 43, 146-155 (2000)] have studied how these enzymes catalyze the hydrolysis of p-nitrophenyl phosphate [PNPP]. Initial-rate data from their experiments at 30°C are shown in the table. From these data, evaluate the Michaelis-Menten parameters, \( v_{\text{max}} \) and \( K_m \), in the Michaelis-Menten rate equation:

\[
v = v_{\text{max}} \left( \frac{[S]_0}{[S]_0 + K_m} \right).
\]

Show all work.

<table>
<thead>
<tr>
<th>[PNPP] (micromole dm(^{-3}))</th>
<th>Initial rate (micromoles dm(^{-3}) s(^{-1}))</th>
<th>1/[PNPP] (dm(^{-3}) micromole(^{-1}))</th>
<th>1/(Initial rate) (s dm(^{-3}) micromole(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.299</td>
<td>0.069</td>
<td>3.344</td>
<td>14.493</td>
</tr>
<tr>
<td>0.5</td>
<td>0.105</td>
<td>2.000</td>
<td>9.524</td>
</tr>
<tr>
<td>0.82</td>
<td>0.15</td>
<td>1.220</td>
<td>6.667</td>
</tr>
<tr>
<td>1.22</td>
<td>0.23</td>
<td>0.820</td>
<td>4.348</td>
</tr>
<tr>
<td>1.75</td>
<td>0.286</td>
<td>0.571</td>
<td>3.497</td>
</tr>
<tr>
<td>2.85</td>
<td>0.333</td>
<td>0.351</td>
<td>3.003</td>
</tr>
<tr>
<td>5</td>
<td>0.4</td>
<td>0.200</td>
<td>2.500</td>
</tr>
<tr>
<td>5.88</td>
<td>0.5</td>
<td>0.170</td>
<td>2.000</td>
</tr>
</tbody>
</table>

A plot of the inverse of the rate versus the inverse of the substrate concentration should be a straight line, from which one can extract the information. In particular, the y intercept is the inverse of \( v_{\text{max}} \). Using the intercept on this graph, then, \( v_{\text{max}} = 0.6680 \) micromole dm\(^{-3}\) s\(^{-1}\).

The slope of the plot gives \( K_m \) when multiplied by \( v_{\text{max}} \). Hence,

\[
K_m = \frac{(0.6680 \, \mu\text{mole dm}^{-3} \, \text{s}^{-1})(3.9252 \, \text{s})}{2.62 \, \mu\text{mole dm}^{-3}}
\]
8. (10 points) Barker et al. (*Anal. Chem.*, 71, 1767 – 1772 (1999).) reported a device consisting of fluorescent-dye-labeled cytochrome c’ supported on colloidal gold particles. The device is intended to be a detector of nitric oxide in biological systems. The basis of the detection is the quenching of the dye’s fluorescence by nitric oxide that interacts with the cytochrome, thus shortening the lifetime of the dye fluorescence. The figure below, modified from one of their figures, shows the fluorescence decay of the dye-labeled cytochrome in the absence of nitric oxide following excitation with a laser pulse. Determine the fluorescence lifetime of the dye in the absence of nitric oxide. [Show all work clearly.]

The fluorescence decay, after the initial excitation, is predicted by theory to be exponential. That is, the fluorescence is predicted to follow the equation

\[ I_f(t) = I_{f,0} e^{-t/\tau_f}, \]

where \( \tau_f \) is the fluorescence lifetime. One may observe that a plot of the natural logarithm of the fluorescence versus time should be linear and obey the following equation:

\[ \ln \left( \frac{I_f}{I_{f,0}} \right) = -\frac{t}{\tau_f}. \]

The plot happens to show the logarithm to the base 10 of the fluorescence versus time. However, these two logarithms are related by the following formula:

\[ \log_{10}(y) = \frac{1}{2.30259} \ln(y). \]

So, the \( \log_{10} \) of the fluorescence would also be expected to be linear and of the form:

\[ \log_{10} \left( \frac{I_f}{I_{f,0}} \right) = \frac{1}{2.30259} \ln \left( \frac{I_f}{I_{f,0}} \right) = -\frac{t}{2.30259 \tau_f}. \]

The red line shown in the figure is an estimated straight line through the data (excluding the part during the excitation with a laser pulse at short times). Its slope is estimated, as shown by the blue lines, to be

\[ \text{slope} = \frac{2.35 - 2.85}{(8-2) \text{ns}} = -0.0833 \text{ ns}^{-1}. \]

From this slope, one easily finds the fluorescence lifetime. Using these numbers gives a value: \( \tau_f = 5.2 \text{ ns} \).

Depending on how one estimated the slope, the value could be between 4.5 ns and 6.0 ns.
9. **(10 points)** Below are statements about wave functions. Decide whether each statement is true (T) or false (F) and indicate by checking the appropriate box.

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>F</td>
<td>1. An acceptable wave function must be a single-valued function of the co-ordinates.</td>
</tr>
<tr>
<td>F</td>
<td>T</td>
<td>2. The value of the wave function at any point in space is the probability that the particle is there.</td>
</tr>
<tr>
<td>T</td>
<td>F</td>
<td>3. The first derivative of the wave function must be continuous at all points in space.</td>
</tr>
<tr>
<td>T</td>
<td>F</td>
<td>4. Wave functions associated with different eigenvalues of an operator must be orthogonal functions.</td>
</tr>
<tr>
<td>F</td>
<td>T</td>
<td>5. All wave functions corresponding to real systems must be real functions of the co-ordinates.</td>
</tr>
</tbody>
</table>
10. (10 points) A model appropriate to an ideal-gas molecule is the particle in a box. To make this more tractable, consider only one dimension (x). For a particle in a state given by the normalized wave function of the particle in a one-dimensional box, \( \Psi_n(x) = \frac{2}{\sqrt{a}} \sin\left(\frac{n\pi x}{a}\right) \) for the state with quantum number \( n \), where \( a \) is the width of the one-dimensional box and \( m \) is the mass of the particle. \( h \) is Planck’s constant. Calculate the expectation value of the position of the particle, \( <x> \), in the state with \( n = 1 \) in terms of the width of the box and any other constants.

This is a straightforward integration problem. One needs to perform a single integral:

\[
<x> = \int_{-\infty}^{\infty} \Psi^* x \Psi \, dx
\]

For a particle in a one-dimensional box, there are three regions. So, the integral may be split into the sum of three integrals.

\[
<x> = \int_{-\infty}^{0} \Psi^* x \Psi \, dx + \int_{0}^{a} \Psi^* x \Psi \, dx + \int_{a}^{\infty} \Psi^* x \Psi \, dx
\]

The first and last integrals are zero because in those regions the wave function is identically zero. The calculation simplifies to determining a single integral.

\[
<x> = \int_{0}^{a} \Psi^* x \Psi \, dx = \int_{0}^{\infty} \frac{2}{\sqrt{a}} \sin\left(\frac{\pi x}{a}\right) x \sqrt{\frac{2}{a}} \sin\left(\frac{\pi x}{a}\right) \, dx
\]

\[
= \frac{2}{a} \int_{0}^{a} x \sin\left(\frac{\pi x}{a}\right) \, dx
\]

This integral is found in the integral table in the Handbook. Substitution gives the following

\[
<x> = \frac{2}{a} \int_{0}^{a} x \sin\left(\frac{\pi x}{a}\right) \, dx = \frac{2}{a} \left\{ \frac{x^2}{4} - \frac{x \sin\left(\frac{2\pi x}{a}\right)}{4\left(\frac{\pi}{a}\right)} - \frac{\cos\left(\frac{2\pi x}{a}\right)}{8\left(\frac{\pi}{a}\right)^2} \right\}^{a}_{0}
\]

\[
= \frac{2}{a} \left\{ \frac{a^2}{4} - \frac{a \sin\left(\frac{2\pi a}{a}\right)}{4\left(\frac{\pi}{a}\right)} - \frac{\cos\left(\frac{2\pi a}{a}\right)}{8\left(\frac{\pi}{a}\right)^2} \right\} - \frac{2}{a} \left\{ \frac{0^2}{4} - \frac{0 \sin\left(\frac{2\pi 0}{a}\right)}{4\left(\frac{\pi}{a}\right)} - \frac{\cos\left(\frac{2\pi 0}{a}\right)}{8\left(\frac{\pi}{a}\right)^2} \right\}
\]

\[
= \frac{2}{a} \left\{ \frac{a^2}{4} - \frac{a \sin(2\pi)}{4\left(\frac{\pi}{a}\right)} - \frac{\cos(2\pi)}{8\left(\frac{\pi}{a}\right)^2} \right\} + \frac{2}{a} \left\{ \frac{\cos(0)}{8\left(\frac{\pi}{a}\right)^2} \right\} = \frac{2}{a} \left\{ \frac{a^2}{4} - 0 - \frac{1}{8\left(\frac{\pi}{a}\right)^2} \right\} + \frac{2}{a} \left\{ \frac{1}{8\left(\frac{\pi}{a}\right)^2} \right\}
\]

\[
= \frac{a}{2}
\]

The average position of the particle is at the exact middle of the box.
11. (10 points) \(\beta\)-carotene, found in many biological systems, contains an extended \(\pi\) network. In particular, a \(\pi\) electron in this molecule can be thought of as a particle in a one-dimensional box.

This molecule has a broad absorption band that has a wavelength of approximately 550 nm. Considering this to be the result of a transition from the \(n = 11\) to \(n = 12\) state of an electron in a one-dimensional box, predict the length of the box (which gives an idea of the length of the conjugated chain).

The transition corresponds to an energy given by the equation

\[
\Delta E = E_2 - E_1 = \frac{h^2}{8ma^2} \left(12^2 - 11^2\right) = \frac{23h^2}{8ma^2}.
\]

Of course, we have the wavelength of the radiation, so we need to convert this to an energy change

\[
\Delta E = \frac{hc}{\lambda}.
\]

Combining these two equations gives

\[
a^2 = \frac{23h\lambda}{8mc} = \frac{23(6.6260693 \times 10^{-34} \text{ Js})(550 \times 10^{-9} \text{ m})}{8(9.1093826 \times 10^{-31} \text{ kg})(2.99792458 \times 10^8 \text{ m s}^{-1})}
\]

\[
= 3.837 \times 10^{-18} \text{ m}^2
\]

Therefore, the predicted length of the conjugated chain is

\[
a = 1.96 \times 10^{-9} \text{ m} = 1.96 \text{ nm}
\]
12. (10 points, extra credit) TV sets were originally based on the fact that a beam of electrons could be directed to a screen containing phosphors. When hit by the electrons, the phosphors in a region (a dot) would light up to produce a “signal”. The actual picture was produced by scanning the electron beam (which was being modulated to produce varying signals for the various regions of a picture) across all the phosphors on the screen (a process called “rastering”).

In displays, one factor that affects the quality is resolution, the ability to distinguish between the position of two adjacent signals. For high resolution, one needs to be able to distinguish signals from phosphors that are typically within about 0.1 mm of each other. In the original TV sets, the electrons were accelerated by the imposition of high voltage, which resulted in the electron having an energy of approximately $1.0 \times 10^4$ eV. In general, the uncertainty in this energy was about 1.0%.

Here is the question you must answer: Does one have to worry about quantum mechanical uncertainty destroying the resolution of a typical television set of this sort?  

[It is not sufficient to answer this question with just a “Yes” or a “No”. You must give a detailed discussion, including calculations, to receive any credit.]

The electron traveling in the evacuated space of the kinescope is essentially a quantum mechanical free particle, the model for which we have solved. In particular, we know that for this particle

$$< p^2 > = 2m < E >$$

$$< p^2 > = 2(9.1093826 \times 10^{-31} \text{kg})(1 \times 10^4 \text{eV}) (96.4853 \times 10^3 \text{J mol}^{-1}) \frac{6.02211415 \times 10^{23} \text{electron mol}^{-1}}{6.02211415 \times 10^{23} \text{mol electron}^{-1}}$$

$$= 2.9190 \times 10^{-49} \text{kg}^2 \text{m}^2 \text{s}^{-2}$$

From this equation, one gets the root-mean-square momentum

$$\sqrt{< p^2 >} = 5.4028 \times 10^{-25} \text{kg m s}^{-1}$$

Because the energy is uncertain, the magnitude of the momentum is also uncertain. The percentage uncertainty in the rms momentum is related to the percentage uncertainty in the energy. Using differential calculus, the percentage uncertainty in the rms momentum is about 0.5%, or $2.701 \times 10^{-27}$ kg m s$^{-1}$.

Heisenberg’s uncertainty principle gives the minimum value of the uncertainty in the position of the electron:

$$\Delta x \geq \frac{\hbar}{2\Delta p} = \frac{6.6260693 \times 10^{-34} \text{J s}}{4\pi(2.701 \times 10^{-27} \text{kg m s}^{-1})} = 1.95 \times 10^{-8} \text{m}$$

This is certainly less than the typical spacing of phosphor dots, so the Heisenberg uncertainty principle is not germane to the resolution limit of the process to any measurable degree.