CHEM 190 and CHEM 290

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Homework No. 9
Due June 7 in class

1. The results of measurements of the rate constant of the decomposition of an organic compound over a range of temperatures are:

T/K	282.3	291.4	304.1	313.6	320.2	331.3	343.8	354.9	363.8	371.7
$k/10^{-3}\mathrm{M}^{-1}\mathrm{s}^{-1}$	.0249	.0691	0.319	0.921	1.95	5.98	19.4	57.8	114.	212.

The temperature dependence of the rate constant is given by the Arrhenius equation

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

or

$$\ln(k) = -\frac{E_a}{RT} + \ln A,$$

in which the activation energy E_a and pre-exponential factor A may be assumed to be constant over the experimental range of temperature. A plot of $\ln(k)$ against $1/T$ should therefore be a straight line.

i) Construct a table of values of $1/T$ and $\ln(k)$, determine the linear least-squares fit to the data assuming only k is in error, and calculate the best values of E_a and A.

ii) Assuming that the errors in $\ln(k)$ are all equal to $\sigma = 0.1$, find estimates of the errors in E_a and A.

2. An engineer wishes to estimate the mean yield of a chemical process based on the yield measurements X_1, X_2, X_3 from three runs of an experiment. Consider the following two estimators of the mean yield of μ:

$$T_1 = \frac{X_1 + X_2 + X_3}{3} \quad \text{(the sample mean)}$$

$$T_2 = \frac{X_1 + 2X_2 + X_3}{4} \quad \text{(a weighted average of the observations)}$$

Which estimator should be preferred, and why ?

3. Kiwi birds are native to New Zealand. They are born exactly one foot tall and grow in one foot intervals. That is, one moment they are one foot tall, and the next they are two feet tall, etc. They are also very rare. An investigator goes to New Zealand and finds four birds. The mean height of the four birds is 4 feet, the median height is 3 feet, and the mode is 2 feet. What are the heights of the four birds?

4. SEE SUPPLEMENTAL PROBLEM 1.

5. SEE SUPPLEMENTAL PROBLEM 2.

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THE FOLLOWING ARE PROBABILITY THEORY SAMPLE TEST PROBLEMS FROM PREVIOUS EXAMS.

1. A basket contains 20 apples of which 4 are rotten. Give numerical answers to the following questions.

   (a) (5 points)
   How many ways can you choose 5 apples out of 20?

   (b) (5 points)
   How many ways are there to choose 5 *good* apples?

   (c) (5 points)
   If you pick 5 apples, what is the probability of picking at least one bad apple?

2. Suppose that you have 3 objects and 7 slots.

   (a) 5 points
   What is the probability that all 3 objects are in the first slot if the objects are *distinguishable*? You can leave your answer in combinatorial form.

   (b) 5 points
   What is the probability that all 3 objects are in the first slot if the objects are *indistinguishable* (multiple occupancy OK)? You can leave your answer in combinatorial form.

   (c) 5 points
   Give a numerical result for the ratio of the relative probabilities, i.e. the ratio of your answer to (a) and (b). If you have done those problems correctly, you should find that the odds of finding all objects in slot 1 are smaller if the objects are distinguishable than if they are indistinguishable.

3. One or more of the following sums valid for $x < 1$ may be helpful in this problem:

$$\sum_{n=0}^{\infty} x^n = \frac{1}{1-x} , \qquad \sum_{n=0}^{\infty} (-1)^n x^n = \frac{1}{1+x}$$

$$\sum_{n=0}^{N} x^n = \frac{1-x^{N+1}}{1-x} , \qquad \sum_{n=1}^{\infty} = \frac{x}{1-x}$$

   Consider the discrete distribution

$$P(r) = (1-a)a^r , \qquad r = 0, 1, 2, \cdots$$

   where a is some fixed parameter smaller than unity. This is the probability of the outcome r in an experiment.

   (a)(5 points)
   Show that the distribution $P(r)$ is normalized.

   (b) (5 points)
   Show that the mean of the distribution is

$$< r >= \frac{a}{(1-a)} .$$

(c) (5 points)
Show that the median of the distribution is

$$r_{med} = \frac{\ln \frac{1}{2}}{\ln a} - 1 \ .$$

(d) (5 points)
If the parameter $a = 1/2$ then the median of the distribution is $r_{med} = 0$. Does this make sense? Why or why not?

4. The wavefunction for the 1s state of the hydrogen atom is

$$\psi(r, \theta, \phi) = \left(\frac{1}{\pi a_0^3} \right)^{1/2} e^{-r/a_0}$$

where a_0 is the Bohr radius. It then follows that the probability density is

$$P(r, \theta, \phi) = \frac{1}{\pi a_0^3} e^{-2r/a_0} \ .$$

This probability density is normalized so that

$$\int \int \int r^2 \sin\theta \ dr \ d\theta \ d\phi P(r, \theta, \phi) = 4\pi \int_0^\infty dr \ r^2 \ P(r, \theta, \phi) = 1$$

where we have noted that the probability density does not depend on the angles and therefore the angular integrals can just be carried out (giving the 4π factor). Calculate the average of the function $f(r) = a_0^2/r^2$ for the hydrogen atom, i.e., calculate the average $\langle (a_0/r)^2 \rangle$. Your answer should be a simple number.