

Chemistry related exercises in mathematics

1. The density function which describes the probability to find an electron in the $1s$ -orbital of the hydrogen atom a certain distance r from the nucleus is given by the equation

$$P(r) = 4 \left(\frac{1}{a_0} \right)^3 e^{-2r/a_0} r^2$$

where a_0 is the so called Bohr radius (equal to 52.9 pm). For what distance, r , does this distribution have a maximum?

Show also that this probability function is normalized, i.e.

$$\int_0^\infty P(r) dr = 1$$

which means that the probability of finding the electron *somewhere* outside the nucleus is one.

2. The vibrational energy of a diatomic molecule can be approximated by the Morse function

$$U(r) = A \left(1 - e^{-B(r-r_0)} \right)^2$$

where A , B , and r_0 are constants. Find the interatomic distance for which U has a minimum.

3. The distribution function describing the probability density of finding a ground state electron in a “one-dimensional” box of length a is given by

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

This is e.g. a model which can be used for electrons in a system of alternating single and double bonds. Find the value of x for which $\psi(x)$ has a maximum, i.e. where the probability is largest to find the electron.

4. The reason that not all substances are gases is that molecules and atoms interact. An often used model to describe the interaction energy between two molecules a distance r apart is the Lennard-Jones potential energy function

$$U(r) = 4\varepsilon \left[\left(\frac{d}{r} \right)^{12} - \left(\frac{d}{r} \right)^6 \right]$$

where d is the size of the molecule and ε is a measure of the interaction energy. Determine whether this function has a maximum, a minimum, or both. Also calculate the value of the function at any extreme points. Try to interpret your result physically.

5. When calculating the osmotic pressure (Π) of a solution, e.g. dissolved salt or sugar in water, one encounters the following function

$$\Pi = -\frac{RT}{V} \ln(1 - x)$$

where R is the gas constant, T is the temperature, and x is the mole fraction of the dissolved substance (essentially the concentration). Find the Maclaurin series of $\ln(1 - x)$, which can be used to rewrite the osmotic pressure in solutions with low concentrations.

6. The bridge between atoms and molecules, and properties like pressure, reaction heat, equilibrium constants etc. is a branch of chemistry and physics called statistical mechanics. The most typical calculation one encounters in a first course is the derivative with respect to temperature of the following types of functions

$$q(T) = \sum_i e^{-E_i/kT}$$

and

$$\ln q(T) = \ln \sum_i e^{-E_i/kT}$$

What are the results after taking the derivative?

7. Einstein suggested in 1905 a model for the heat capacity of an atomic crystal (i.e. how much energy in the form of heating that is needed to raise the temperature of the substance). He pictured the crystal as a lot of atoms vibrating around their equilibrium positions. For a crystal consisting of N atoms, one can define a function $Q(T)$ - the partition function, from which the heat capacity can be calculated.

$$Q = e^{-U_0/kT} \left(\frac{e^{-h\nu_0/2kT}}{1 - e^{-h\nu_0/kT}} \right)^{3N}$$

Keeping the volume of the crystal constant, the heat capacity C_V can now be calculated as

$$C_V = \frac{dU(T)}{dT}$$

with $U(T)$ given by

$$U(T) = kT^2 \left(\frac{d \ln Q(T)}{dT} \right)$$

The constant U_0 is the heat needed to transfer the crystal to a gas at zero kelvin, $k = 1.38066 \cdot 10^{-23}$ J/mol (Boltzmann's constant), and $h = 6.626 \cdot 10^{-34}$ J s (Planck's constant). Calculate the heat capacity for diamond at 298 K if $\nu_0 = 2.75 \cdot 10^{13}$ Hz is the vibration frequency for the atoms in the crystal.

8. The pressure-volume work done when a gas expands or is compressed is given by

$$w = - \int_{V_1}^{V_2} P(V) dV$$

For many gases, a good approximation for $P(V)$ is the van der Waals' "equation of state"

$$P = \frac{nRT}{V - nb} - \frac{an^2}{V^2}$$

where n is the number of moles of the gas, $R = 8.314 \text{ J/(K mol)}$ and a and b are constants whose values depend on the gas.

Calculate the work when one mole ($n = 1$) of SO_2 at 300 K is compressed from $V_1 = 180 \cdot 10^{-3} \text{ m}^3$ to $V_1 = 60 \cdot 10^{-3} \text{ m}^3$. For sulphur dioxide $a = 0.1381$ and $b = 3.219 \cdot 10^{-5}$ in appropriate units.

9. One can determine when a chemical reaction, at a constant pressure, has reached equilibrium by looking at the change in a quantity called the Gibbs free energy (G). To be able to predict how the outcome of a chemical reaction varies with temperature, one can use one form of the Gibbs-Helmholtz equation

$$\frac{d(\Delta G/T)}{dT} = -\frac{a + bT + cT^2}{T^2} \quad (1)$$

Derive an expression for ΔG as a function of T , if $\Delta G = \Delta G_1$ at the temperature T_1 .

10. (a) The rate of many chemical reactions is experimentally found to be proportional to the concentration of reactant, $[A]$, at any time t during the reaction (a first order reaction)

$$\frac{d[A]}{dt} = -k[A] \quad (2)$$

where we have a minus sign since the concentration of the reactant $[A]$ is decreasing with time. If the initial concentration of $[A]$ is denoted $[A]_0$, find an expression for $[A]$ as a function of time.

- (b) Given the following data for the decomposition of N_2O_5 in liquid bromine, determine the rate constant k by plotting the data so that a straight line results.

$t/(\text{s})$	0	200	400	600	1000
$[\text{N}_2\text{O}_5]/\text{M}$	0.110	0.073	0.048	0.032	0.014