Problem Set 1: Mathematics Review for Physical Chemistry

HCHE 321L: Physical Chemistry 1

Due Date: August 23$^{\text{rd}}$, 2017

Problem 1

Consider a general function of the following form:

$$z(x, y) = ax^2 + bxy + cy^2 \tag{1}$$

(a) Express the function z in terms of x and u, where $u = xy$

(b) Find the partial derivative:

$$\left(\frac{\partial z}{\partial x}\right)_y \tag{2}$$

(c) Find the partial derivative:

$$\left(\frac{\partial z}{\partial x}\right)_u \tag{3}$$

Problem 2

Consider the following vectors: $\mathbf{A} = \mathbf{i}A_x + \mathbf{j}A_y + \mathbf{k}A_z$ and $\mathbf{B} = \mathbf{i}B_x + \mathbf{j}B_y + \mathbf{k}B_z$.

(a) Provide an expression for the *scalar product* of the two vectors, i.e. solve $\mathbf{A} \cdot \mathbf{B}$.

(b) Provide an expression for the *magnitude* of each vector, i.e. solve $|\mathbf{A}|$ and $|\mathbf{B}|$.

(c) Use the information you solved for in parts (a) and (b) in order to find the angle between $\mathbf{A}$ and $\mathbf{B}$.

Problem 3

Statistical mechanics is a branch of physical chemistry that uses probability to describe the physics of many molecules! Using its power, we can define pressure (P) and internal energy (U) as a function of temperature (T), using a statistical variable known as the partition function (Q):

$$P(T) = ke^{-Q/T} \tag{4}$$

$$U(T) = \frac{Nh\nu}{e^{h\nu/k_B T} - 1} \tag{5}$$

(a) Find dP/dT

(b) The heat capacity (C) can be defined as:

$$C = \frac{dU}{dT} \tag{6}$$

show that the heat capacity can be expressed as:

$$C = Nk_B \left(\frac{h\nu}{k_B T}\right)^2 \frac{e^{h\nu/k_B T}}{(e^{h\nu/k_B T} - 1)^2} \tag{7}$$

(c) Find the limit of the heat capacity as T→0 and as T→∞

Problem 4

A useful identity for partial derivatives is known as the *reciprocal identity*, this states that a derivative is equal to the reciprocal of the derivative with the roles of dependent and independent variables reversed

$$\left(\frac{\partial y}{\partial x}\right)_{z,u} = \frac{1}{(\partial x/\partial y)_{z,u}} \tag{8}$$

The same variables must be held constant in the two derivatives. Show that the reciprocal identity is satisfied by $(\partial z/\partial x)_y$ and $(\partial x/\partial z)_y$ if

$$z = \sin\left(\frac{x}{y}\right) \tag{9}$$

Problem 5

For a general function y, that depends on n independent variables: x_1, x_2, ..., x_n, the *total differential* of this function can be expressed as:

$$dy = \sum_{i=1}^{n} \left(\frac{\partial y}{\partial x_i}\right)_{x'} dx_i \tag{10}$$

where the symbol x' stands for keeping all of the variables constant except for x_i in the differentiation.

(a) Consider pressure (P) where $P(V, T, n)$, provide an expression for the total differential dP

(b) Assuming an ideal gas, $P = nRT/V$. Provide an expression for dP of an ideal gas.

Problem 6

Consider the following indefinite integral:

$$\int \frac{6x - 30}{x^2 + 3x + 2} dx \tag{11}$$

(a) Show that this integral can be re-expressed in the following way:

$$\int \frac{6x - 30}{x^2 + 3x + 2} dx = \int \frac{42}{x+2} dx - \int \frac{36}{x+1} dx \tag{12}$$

HINT: Must use method of partial fractions.

(b) Solve for the indefinite integrals on the right hand side of Equation 12