系別：化學學系(化學組)　　科目：物　理　化　學

考試日期：2 月 28 日(星期一) 第 4 節　　本試題共　六　大題，　三　頁

本試題雙面印刷

1)

Based on the physical phenomena of the blackbody radiation we realized that the frequency distribution of the emitted blackbody radiation be described by the function $R(\nu)$, where $R(\nu)\,d\nu$ is the energy with frequency in the range ν to $\nu + d\nu$ that is radiated per unit time and per unit surface area. In June 1900 Lord Rayleigh attempted to derive the theoretical expression for the $R(\nu)$ as follow:

$$R(\nu) = (2\pi kT/c^2)\,\nu^2. \qquad \text{Eq. 1-1}$$

On October 1900, the physicist Max Planck announced his derivation of a formula as follows:

$$R(\nu) = (2\pi h/c^2)\,(\nu^3/e^{h\nu/kt}-1). \qquad \text{Eq 1-2}$$

Please make a statement to describe a) both equations Eq. 1-1 and Eq. 1-2 in terms of their different basics (10%), b) how this difference leads to the important concept of the energy quantization. (5%) and c) finally how the value of planck's constant *h* is obtained. (5%)

2)

It was realized that the solution of the Schrödinger equation for a particle of mass m free to move parallel to the X-axis with zero potential energy, that is $V(x)= 0$, is given as follows:

$$\psi = A\,e^{ikx} + Be^{-ikx} \text{ and } E = k^2\hbar^2/2m \qquad \text{Eq. 2-1}$$

where A and B are constants.

a) Please verify that the $\psi = A\,e^{ikx} + Be^{-ikx}$ is indeed a solution of the Schrödinger equation for a particle of mass m free to move parallel to the X-axis with zero potential energy.(5%)

Having determined the wavefunction $\psi = A\,e^{ikx} + Be^{-ikx}$ now we are in a position to calculate the probability density $|\psi|^2$.

b) Please evaluate the probability density $|\psi|^2$ by assuming that either B= 0 or A=0, then make your conclusion about the probability of finding the particle. (5%)

Consider the operators d/dx and d^2/dx^2. Is the function $\psi = A\,e^{ikx} + Be^{-ikx}$ an eigenfunction of these operators? If so, what are the eigenvalues? Note that A, B and k are real numbers.(5%)

3)

It is realized that for a particle of mass m freely move anywhere on the surface of a sphere of radius r is the rotation of m in three dimensions.

a) If the laplacian ∇^2 in spherical polar coordinates is written as follows:

$$\nabla^2 = \frac{\partial}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\Lambda^2 \qquad \text{Eq. 3-1}$$

where the legendrian, Λ^2 is

$$\Lambda^2 = \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\sin\theta\frac{\partial}{\partial\theta} \qquad \text{Eq. 3-2}$$

Please write the Schrodinger equation for rotational motion in three dimensions in which the *r* is constant. (5%)

b) Please use the separation of variables method to transform the above Schrodinger equation into two parts, that is, the ϕ dependent equation and the θ dependent equation, in order to obtain two types of quantum numbers by solving these two equations, respectively. Then please describe the correlation between these two types of quantum numbers. (10%)

4)

Kinetic experiments yield the concentration [A].of reacting species as functions of time at a fixed temperature. Suppose the reaction aA -→ product is the first order with r = k [A] and the rate law is as follows:

$$r = (-1/a)\, d[A]/dt = k[A]. \qquad \text{Eq. 4-1}$$

a) Please derive expression for the concentration [A] as a function of time leading to the exact expression of the rate law. (5%)

b) Please rearrange the exact expression for the rate law to illustrate the linear relationship between $\ln([A]_0/[A])$ versus t with slope ak.(5%)

c) Finally, please derive the exact expression of the reaction's half-life $t_{1/2}$. (5%)

5)

a) Calculate

$$\left(\frac{\partial f}{\partial x}\right)_y \quad \left(\frac{\partial f}{\partial y}\right)_x \quad \left(\frac{\partial^2 f}{\partial x^2}\right)_y \quad \left(\frac{\partial^2 f}{\partial y^2}\right)_x \quad \left(\frac{\partial\left(\frac{\partial f}{\partial x}\right)_y}{\partial y}\right)_x \text{ and } \left(\frac{\partial\left(\frac{\partial f}{\partial y}\right)_x}{\partial x}\right)_y$$

For the function $f(x,y) = ye^x + xy + x\ln y$ (10%)

b) Determine if f(x,y) is a state function of the variables x and y.(5%)

c) if f(x,y) is a state function of the variables x and y, what is the total differential df ?(5%).

6)

It was realized that the Boltzmann distribution is written as the fraction of molecules in the state i, that is, $p_i = n! / N$, and it is expressed as $e^{-\beta\varepsilon i} / q$.

a) Please give the name for the q and write the exact expression for the q. (5%)

b) Based on your expression for the q, please write the q of the a linear molecule treated as rigid rotor. (5%) **(The energy level of a linear rotor are hcBJ(J+1) with J=0,1,2,3,… and it consists of 2J +1 degenerate states.)**

c) Imagine that you have a uniform ladder of energy levels which is similar to the vibrational energy level of a diatomic molecule in the harmonic approximation. c) Please derive the formula for the q. (5%) **(You probably need this mathematical expression $1+X+X^2+X^3+X^4+ \ldots = 1/(1-X)$).**