Physical Chemistry

Cumulative Exam

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This exam is on your understanding of the principles of probability as they apply to two of the three important branches of physical chemistry: quantum mechanics and statistical mechanics

1. The probability that a system will occupy an energy state with energy E is proportional to exp[-E/RT] if E is given in units of energy per mole. Consider a simple system having only four possible energy states that we denote as States 1, 2, 3, 4. The energies of these states are:

$E_1 = 0\ J\ mol^{-1}$ $E_2 = 1000\ J\ mol^{-1}$ $E_3 = 2000\ J\ mol^{-1}$ $E_4 = 3000\ J\ mol^{-1}$

(a) Obtain the <u>normalized</u> probability distribution for the system in state i. Evaluate the normalization constant if T = 298 K. $R = 8.314\ J\ K^{-1}\ mol^{-1}$ Identify the reciprocal of the normalization constant with an important quantity in statistical mechanics.

(b) Calculate the average energy per system that a large number of such systems would have at 298 K.

(c) Determine which energy state makes the greatest contribution to the average energy.

(d) Determine which energy state is the most heavily populated.

(e) Determine the probability that the combined energy of two separate systems described by the given probability distribution will add to 3000 joules.

(f) Compute the average total energy the two systems in (e) will have at 298 K. What relationship does this result have to that obtained in (b)?

2. The average energy of two systems described in problem 1 is exactly twice the average energy of a single system. This is the general property of any system in which the probability that the system will occupy a state of energy E is proportional to exp[-E/RT]. Suppose such as system has M possible energy states.

(a) Obtain an expression for the average energy of one such system, $\langle E \rangle_1$.

(b) Show that the average energy for N such systems is just $N\langle E \rangle_1$.

3. The wavefunctions of a harmonic oscillator are given by:

$\Psi_0 (x) = [\alpha/\pi]^{1/4} \exp[-\alpha x^2/2]$ where $\alpha = (\mu k)^{1/2}/\hbar$ $\nu = (1/2\pi)(k/\mu)^{1/2}$

$\Psi_1 (x) = [4\alpha^3/\pi]^{1/4}\, x \exp[-\alpha x^2/2]$ $\hbar = 1.055 \times 10^{-34}$ J s

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(a) Compute the probability that a quantum harmonic oscillator in its ground state with a fundamental vibrational frequency equal to $1.350 \times 10^{14}\ s^{-1}$ and a reduced mass equal to that of H_2 will be found in the classically forbidden region of space. Hint: At the classical turning points, $x = x_t$, all of the energy is in the form of potential energy. Find x_t by equating the total energy to the potential energy at the turning points.