Benha university	4th year students	Date : 30-12-2014
Faculty of science	Special chemistry	Time: 2 hours
Chemistry department	Quantum and statistical thermodynamics	

Answer for only two questions:

4- **A)** Derive expressions for the rotational contribution to the following thermodynamic quantities for a diatomic molecule: **(i)** the pressure **(ii)** the entropy (10 marks)

(i) The pressure is calculated by taking the volume derivative
of the partition function. However, the rotational partition
function does not depend on the volume. Therefore the rotational
contribution to the pressure is zero.

(ii) To derive an expression for the entropy, begin by writing the
definition in terms of the total partition function, and then
introduce the rotational partition function:

$$S = k_B T \left(\frac{\partial \ln Q}{\partial T} \right)_V + k_B \ln Q \qquad Q = \left(\frac{T}{\sigma \theta_r} \right)^N$$

$$\therefore S = N k_B T \left(\frac{\partial \ln T}{\partial T} \right)_V + N k_B \ln \left(\frac{T}{\sigma \theta_r} \right) = N k_B + N k_B \ln \left(\frac{T}{\sigma \theta_r} \right)$$

B) Calculate (i) the de Broglie wavelength and (ii) the translational partition function for an atom of Br (mass=79.90 g mol^{-1}) at 500K when occupying a volume of 35 dm^3.

(i) In the following parts, remember to use only SI units, (a) The de Broglie wavelength is given by:

$$\lambda = \left(\frac{h^2}{2\pi m k_B T} \right)^{1/2} = \left(\frac{\left(6.6262 \times 10^{-34} \text{ J s} \right)^2}{2\pi \left(\frac{79.90 \times 10^{-3}}{6.022 \times 10^{23}} \text{ kg} \right) \left(1.38066 \times 10^{-23} \text{ J K}^{-1} \right) \left(500 \text{ K} \right)} \right)^{1/2}$$

$$= 8.735 \times 10^{-12} \text{ m}$$

(10 marks)

(ii) To calculate the translational partition function we can use the de Broglie wavelength:

$$q^T = \lambda^{-3}V = \left(8.735\times10^{-12}\ \text{m}\right)^{-3}\left(35\times10^{-3}\ \text{m}^3\right) = 5.25\times10^{31}$$

5-   **A)** Show that the heat capacity at constant volume can be expressed as:

$$C_V = \frac{\left\langle (\delta U)^2 \right\rangle}{k_B T^2}$$

(10 marks)

To perform the differentiation we must use the quotient rule to handle the fraction, followed by the chain rule to deal with the individual terms:

$$C_V = \frac{\frac{\partial}{\partial T}\left(\sum_i U_i \exp(-U_i/k_B T)\right)}{\sum_i \exp(-U_i/k_B T)} - \frac{\left(\sum_i U_i \exp(-U_i/k_B T)\right)}{\left(\sum_i \exp(-U_i/k_B T)\right)^2}\frac{\partial}{\partial T}\left(\sum_i \exp(-U_i/k_B T)\right)$$

$$= \frac{\sum_i \frac{U_i^2}{k_B T^2}\exp(-U_i/k_B T)}{\sum_i \exp(-U_i/k_B T)} - \frac{\left(\sum_i U_i \exp(-U_i/k_B T)\right)}{\left(\sum_i \exp(-U_i/k_B T)\right)^2}\left(\sum_i \frac{U_i}{k_B T^2}\exp(-U_i/k_B T)\right)$$

$$= \frac{1}{k_B T^2}\left[\frac{\sum_i U_i^2 \exp(-U_i/k_B T)}{\sum_i \exp(-U_i/k_B T)} - \left(\frac{\sum_i U_i \exp(-U_i/k_B T)}{\sum_i \exp(-U_i/k_B T)}\right)^2\right]$$

The first and second terms in the outer bracket can be identified as and by definition. Hence we arrive at the desired result:

$$C_V = \frac{\left\langle U^2 \right\rangle - \left\langle U \right\rangle^2}{k_B T^2}$$

Here the key task is to manipulate the numerator. Starting from the definition of δ(7 and taking its square:

$$(\delta U)^2 = \left(U - \langle U \rangle\right)^2 = U^2 - 2U\langle U \rangle + \langle U \rangle^2$$

Now taking the average of this quantity leads to:

$$\left\langle (\delta U)^2 \right\rangle = \langle U^2 \rangle - 2\langle U \rangle\langle U \rangle + \langle U \rangle^2 = \langle U^2 \rangle - \langle U \rangle^2$$

Substituting for the numerator in the result of the previous problem yields the desired result:

$$C_V = \frac{\left\langle (\delta U)^2 \right\rangle}{k_B T^2}$$

B) Calculate the electronic partition function for the OH radical at 298 K, given that there are two doublet electronic states separted by 139.7 cm^{-1} (10 marks)

The electronic partition function is calculated by a direct sum over the levels, remembering to allow for the degeneracies. Also, the energy separation must be convert to J:

$$q^E = 2\exp(-0) + 2\exp\left(-\frac{139.7 \times 2.9979 \times 10^{10} \times 6.6262 \times 10^{-34}}{1.38066 \times 10^{-23} \times 298}\right)$$

$$= 2 + 1.0188 = 3.019$$

6- **A)** A system consists of a set of uniformly spaced energy levels of separation 1×10^{-20} J, starting from a first level which has an energy of 0 J. eight particles are placed within this system with a total energy of 6×10^{-20} J. **(i)** how many possible states are there that satisfy these requirements? **(ii)** which state is the most probable?

7- (15 marks)

(i) There are a total of 11 distinct configurations that are possible. where the occupancies are listed for each level commencing with the ground state, the configurations are:

1	(7,0,0,0,0,0,1)	$W = 8$
2	(6,1,0,0,0,1,0)	$W = 56$
3	(6,0,1,0,1,0,0)	$W = 56$
4	(6,0,0,2,0,0,0)	$W = 28$
5	(5,2,0,0,1,0,0)	$W = 168$
6	(5,1,1,1,0,0,0)	$W = 336$
7	(5,0,3,0,0,0,0)	$W = 112$
8	(4,3,0,1,0,0,0)	$W = 560$
9	(4,2,2,0,0,0,0)	$W = 420$
10	(3,4,1,0,0,0,0)	$W = 560$
11	(2,6,0,0,0,0,0)	$W = 28$

(ii) The number of microstates is listed for each configuration above. The state(s) with the greatest number of microstates will maximize the entropy and thus lead to the lowest free energy. Hence we can see that there are two states which will be equally most probable, both having 560 microstates:

(4,3,0,1,0,0,0) and (3,4,1,0,0,0,0)

B) A gas is composed of three atoms of type A and four atoms of type B, which have atomic partition functions of q_A and q_B respectively. What is the total partition function for this system? (5 marks)

We have to consider the two types of atoms separately, since A and B are distinguishable from each other. Hence we obtain:

$$Q = \left(\frac{q_A{}^3}{3!}\right)\left(\frac{q_B{}^4}{4!}\right) = \frac{q_A{}^3 q_B{}^4}{144}$$

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h(planck constant)=6.6262×10^{-34} J s, K_B(Boltzmann's constant)= 1.38066×10^{-23} J K^{-1}

C(speed of light) $= 2.9979\times 10^{10}$ cm s^{-1}

Best Wishes

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