أ.د. أحمد سعيد شلبي قسم الكيمياء كليه العلوم جامعه بنها امتحان ثالثه كيمياء خاصه ميكانيكا احصائيه
Prof.Dr. Ahmad S. Shalabi

Benha University — 3rd year Students — Date : 29-12-2013
Faculty of Science — Special Chemistry — Time : 3 hours

Chemistry Department
Staistical Mechanics

**ANSWER THREE QUESTIONS ONLY**

1. **Based on the kinetic theory of gases, derive an expression for the translational energy $E_t$ of one mole of a gas.**

2. **Write an expression for the Maxwell – Boltzman law of the distribution of energy.**

3. **How the entropy of a solid is determined when exists in two forms $\alpha$ (high temperature), and $\beta$ ( low temperature) ?**

4. **Calculate the vibrational partition function of :**
   **(i) molecular hydrogen**
   **(ii) molecular chlorine**
   **at 300 $^oK$ , assuming them to be harmonic oscillators.**
   **[ $\omega$ of $H_2$ is 4405 $cm^{-1}$ - $\omega$ of $Cl_2$ is 565 $cm^{-1}$ - $hc\omega/KT = 1.439\omega/T$ ]**

**GOOD LUCK**

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**MODEL ANSWERS**

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**1-**

**The Kinetic Theory of Gases**

Ideal gas law

$$PV = (1/3)\ Nmc^2$$

**P** : the pressure of the gas

**V** : the volume

**N** : the number of molecules

**m** : the mass of the molecules

$c^2$ : the mean square of the velocities of the molecules

at the experimental temperature

Since the equation of state of one mol of an ideal gas is

$$PV = RT$$

$$(1/3)Nmc^2 = RT$$

$$1/2 \quad Nmc^2 = 3/2 \quad RT$$

**N** : Avogadro's number i.e the number of molecules in one mole.

Since the kinetic energy of translation per molecule is

$$1/2 \quad mc^2$$

it follows that

$$E_{tr} = 1/2 \; Nmc^2 = 3/2 \; RT$$

Where $\mathbf{E_{tr}}$ is the total translational energy of the one mol of the gas.

**2-**

**The Partition Function**

. At each temperature there is a particular distribution of the total energy of a gas among its constituent molecules. Let $\boldsymbol{\epsilon_i}$ represents the energy, in excess of the lowest energy state ( zero point vibrational energy) at absolute zero .

Suppose $\mathbf{N_0}$ is the number of molecules in the lowest energy state $\boldsymbol{\epsilon_0}$ , and $\mathbf{N_i}$ is the number of molecules in the energy state $\boldsymbol{\epsilon_i}$ .

The energy distribution among the molecules at constant volume and absolute temperature, is

$$N_i = N_0 \; e^{-\epsilon \;/ KT}$$

where **K** is the **Boltzman constant**, **K = R/N** , **R** is the gas constant and **N** is the Avogadro number.

The foregoing expression is **the Maxwell-Boltzman law** of the distribution of energy derived from classical mechanics.

Introducing the statistical weight factor **g** , representing the number of possible quantum states having the same, or almost the same, energy $\epsilon_i$ , the appropriate form of the energy distribution law is

$$N_i = \text{—} \; g_i \, e^{-\epsilon \;/KT} \quad *$$

where $g_0$ is the statistical weight factor of the lowest energy level.

**3-**

**Tests of the Third Law of Thermodynamics**

Entropies calculated on the basis of the third law in the manner described above are usually in complete agreement with those derived from statistical considerations.

When a solid exists in two or more forms, e.g $\alpha$ (high temperature form) above the transition point and $\beta$ (low temperature form) below the transition point, the entropy of the $\alpha$ form is obtained by measuring the heat capacities of the β- form up to the β → α transition point. The entropy obtained from these results are then added to the entropy of the transition to the α- form to give the entropy of the α- form.

**α- form**

$$\mathbf{S = \int C_p/T \; dT}$$

**T** **Transition point**

**β → α**

$$\mathbf{S = \int C_p/T \; dT}$$

**β- form**

**4-**

**(i)** $H_2$

$$Q_V = \left(1 - e^{-1.439\ \omega/T}\right)^{-1}$$

$$= \left(1 - e^{-1.439\ x\ 4405/300}\right)^{-1}$$

$$= \left(1 - e^{-21.31}\right)^{-1}$$

$$= 1.000$$

**(ii)** $Cl_2$

$$Q_V = \left(1 - e^{-1.439\ \omega/T}\right)^{-1}$$

$$= \left(1 - e^{-1.439\ x\ 565/300}\right)^{-1}$$

$$= \left(1 - e^{-2.710}\right)^{-1}$$

$$= 1.072$$