PERIODIC PROPERTIES

Ques1) Explain the variation of Ionisation Enthalpy in a group and period.

Ques2) Describe the electronegativity and its applications with examples.

Ques3) C shows +4 oxidation state like Pb. Pb is more stable than C. Why?

ENTROPY

→ Derivations of the following

a) $dG = VdP - SdT$
b) Claypeyron - Clausius Equation
c) Gibbs - Helmholtz Equation.
d) Derivations of Maxwell's equations.

→ Important Examples (attatched below).

SPECTROSCOPY

Important Topics

- Franck - Cordon Principle, Chromophores, Auxochromes, Absorption and intensity shifts. Pg-(983-985)
- Types of vibrations and numericall associated (stretching and bending). Refer pg-(999-1000)

Ques1) What is fermi resonance?
Ques2) Derivation of - Reduced mass of molecule $\mu = \frac{m_1 m_2}{m_1 + m_2}$.
- Rotational constant B

(*) Practice all the solved examples and practice problems.

Solved examples

1. Calculate the free energy change when 4 moles of an ideal gas expands from a pressure of 10 to 1 atm at 25 °C.

Solution

$$\Delta G = 2.303\ nRT\log\frac{P_2}{P_1}$$

Here, n = 4 moles; $R = 8.314\ J\ K^{-1}\ mol^{-1}$; T = 273 + 25 = 298 K; P_1 = 10 atm; P_2 = 1 atm.

$$\Delta G = 2.303\times4\times8.314\times298\ \log\frac{1}{10}$$
$$= -22823.39\ J$$

2. ΔG for a reaction at 300 K is –16 kcal; ΔH for the reaction is –10 kcal. What is the entropy of the reaction? What will be ΔG at 330 K?

Solution

(i) $\Delta G = \Delta H - T\Delta S$

or $$\Delta S = \frac{\Delta H - \Delta G}{T} = \frac{-10\ kcal + 16\ kcal}{300\,K} = 0.02\ kcal\,K^{-1} = 20\ cal\,K^{-1}$$

(ii) ΔG at 330 K = $\Delta H - T\Delta S$

$$= -10\ kcal - 330\ K \times 0.02\ kcal\ K^{-1} = -16.6\ kcal.$$

3. Calculate ΔG for the conversion of 1 mole of water at 100 °C and 1 atm to steam at 100 °C and 0.5 atm pressures.

Solution

ΔG = (ΔG for the conversion of H_2O (l) at 100 °C and 1 atm to steam at 100 °C and 1 atm). + (ΔG for the transition of steam at 100 °C from 1 atm to 0.5 atm).

The first term on the RHS is zero, as H_2O (l) and H_2O (g) are in equilibrium at 100 °C and 1 atm pressure.

The second term is = $2.303\ nRT\ \log\frac{P_2}{P_1}$

$$\Delta G = 2.303\times1\times1.987\times373\times\log_{10}\frac{0.5}{1}$$

$$= 2.303 \times 1\times 1.987 \times 373 \times (-0.3010)$$

$$= -513.82\ cal$$

Practice problems

1. 4 mole of an ideal gas is compressed isothermally at 300 K from $2.02 \times 10^5\ N\ m^{-2}$ to $4.04 \times 10^5\ N\ m^{-2}$ pressure. Calculate the free energy change for the process. [Ans 6916.63 J]

2. One mole of an ideal gas at 27 °C expands isothermally and reversibly from initial volume of 2 dm^3 to a final volume of 20 dm^3 against a pressure that is gradually reduced. Calculate q, w, ΔE, ΔH, ΔA, ΔG and ΔS.

[Ans $q = 5744\ J\ mol^{-1}$; $w = -5744\ J\ mol^{-1}$; ΔE= 0; ΔH= 0; $\Delta A = -5744\ J\ mol^{-1}$.
$\Delta G = -5744\ J\ mol^{-1}$ and $\Delta S = 19.15\ J\ K^{-1}\ mol^{-1}$]

3. Calculate ΔG for the formation of H_2O (l) from its elements at 25 °C. $\Delta H_f = -286$ kJ. Entropies of H_2 (g), O_2 (g) and H_2O (g) are 130.6, 205.0 and 70.3 $J\ K^{-1}\ mol^{-1}$, respectively. [Ans ΔG = –237.5 kJ]

Solved examples

1. Calculate the entropy of mixing of 1 mole of N_2 and 2 moles of O_2, assuming the gases to be ideal. Express the result in S.I. units.

Solution

$$\Delta S_{\text{mix}} \text{ per mole} = -2.303R\left[n_1 \log X_1 + n_2 \log X_2\right]$$

$$X_1 = \frac{\text{moles of } N_2}{\text{Total number of moles}} = \frac{1}{3}; X_2 = \frac{\text{moles of } O_2}{\text{Total number of moles}} = \frac{2}{3}$$

$$\begin{aligned}\Delta S_{\text{mix}} &= -2.303 \times 8.314\left[\frac{1}{3}\log\frac{1}{3} + \frac{2}{3}\log\frac{2}{3}\right] \text{J K}^{-1}\\ &= +2.303 \times 8.314\left[\frac{1}{3}\log 3 + \frac{2}{3}\log\frac{3}{2}\right] \text{J K}^{-1}\\ &= 2.303 \times 8.314(0.1590 + 0.1174) \text{ J K}^{-1}\\ &= 5.29 \text{ J K}^{-1}\end{aligned}$$

$$\text{for 3 moles } \Delta S_{\text{mix}} = 3 \times 5.29 = 15.87 \text{ J K}^{-1}$$

2. At NTP, 2.8 L of oxygen were mixed with 19.6 L of hydrogen. Calculate the increase in entropy, assuming ideal gas behavior.

Solution

Here,

$$n_1 = \frac{2.8 \text{ L}}{22.4 \text{ L mol}^{-1}} = 0.125 \text{ mol}; \quad n_2 = \frac{19.6 \text{L}}{22.4 \text{ L mol}^{-1}} = 0.875 \text{ mol}$$

$$X_1 = \frac{0.125}{0.125 + 0.875} = 0.125 \text{ and } X_2 = \frac{0.875}{0.125 + 0.875} = 0.875$$

$$\begin{aligned}\Delta S_{\text{mixing}} &= -R \times 2.303\left[n_1 \log X_1 + n_2 \log X_2\right]\\ &= -8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 2.303 \,[0.125 \text{ mol} \log 0.125 + 0.875 \text{ mol} \log 0.875]\\ &= -8.314 \times 2.303\,[-0.1129 - 0.0507]\\ &= 8.314 \times 2.303 \times (-0.1636) = 3.132 \text{ J K}^{-1}\end{aligned}$$

3. The mixing of gases is always accompanied by an increase in entropy. Show that in the formation of a binary mixture of two ideal gases the maximum entropy increase results when $X_1 = X_2 = 0.5$

Solution

For a binary mixture the entropy per mole of the mixture formed is given by

$$\begin{aligned}\Delta S_{\text{mixing}} &= -R\left[X_1 \ln X_1 + X_2 \ln X_2\right]\\ &= -R\left[X_1 \ln X_1 + (1 - X_1)\ln(1 - X_1)\right]\end{aligned}$$

For entropy of mixing to be maximum, the first derivative $\frac{\delta(\Delta S_{\text{mixing}})}{\delta X_1}$ should be zero and the second derivative should be negative. Differentiating ΔS_{mixing} with respect to X_1 we get

$$\frac{\delta(\Delta S_{\text{mixing}})}{\delta X_1} = -R\left[\ln X_1 + \frac{X_1}{X_1} + \frac{1 - X_1}{1 - X_1}(-1) + (-1)\ln(1 - X_1)\right]$$

$$-R(\ln X_1 + 1 - 1) - \ln(1 - X_1) = 0$$

$$\text{or } \ln X_1 + 1 - 1 - \ln(1 - X_1) = 0$$

$$\text{or } \ln\frac{X_1}{1 - X_1} = 0 \quad \text{or} \quad X_1 = 1 - X_1$$

$$2X_1 = 1 \quad X_1 = 1/2 = 0.5$$

And hence $X_2 = 1–0.5 = 0.5$.

Practice problems

1. 1 mole of H_2 and 9 moles of N_2 are mixed at 298 K and 1 atmosphere. Assuming the ideal behavior of the gas, calculate the entropy of mixing per mole of the mixture formed.

[Ans 2.704 J K^{-1} mol^{-1}]

$$\Delta A = \Delta E + T\left(\frac{}{\partial T}\right)_V \qquad (14)$$

Solved problems

1. For the following reaction

$N_2(g) + 3\,H_2(g) \rightarrow 2NH_3\,(g)$

The free energy change at 25 °C and 35 °C are –3.98 and – 3.37 kcal. Calculate the heat of reaction at 35 °C.

Solution

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

$$\text{also}\left(\frac{\partial \Delta G}{\partial T}\right)_P = \frac{G_2 - G_1}{T_2 - T_1}$$

Here $G_1 = -3.98$ kcal; $G_2 = -3.37$ kcal

$T_1 = 273 + 25 = 298\,K$; $T_2 = 273 + 35 = 308\,K$

$$\therefore \left(\frac{\partial \Delta G}{\partial T}\right)_P = \frac{-3.37 - (-3.98)}{308 - 298} = \frac{0.61}{10} = 0.061$$

At 35 °C $\Delta G = -3.37$ kcal; T = 308 K.

$$-3.37 = \Delta H + 308(0.061)$$
$$\Delta H = -3.37 - 18.79 = -22.16 \text{ kcal}$$

2. For the following reaction

$H_2\,(g) + ½\,O_2\,(g) \rightarrow H_2O\,(l)$

The value of enthalpy change and free energy change are –68.32 and –56.69 kcal respectively at 25 °C. Calculate the value of free energy change at 30 °C.

Solution

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_P$$

Here $\Delta G = -56.69$ kcal; $\Delta H = -68.32$ kcal $T = 273 + 25 = 298\,K$

$$\therefore \left(\frac{\partial \Delta G}{\partial T}\right)_P = \frac{-56.69 + 68.32}{298} = 0.039$$

Assuming that $\left(\frac{\partial \Delta G}{\partial T}\right)_P$ remains constant over this range of temperature, at 30 °C we can write

$$\Delta G = -68.32 + 303 \times 0.039$$
$$= -68.32 + 11.81$$
$$= -56.51 \text{ kcal}$$

Practice problems

1. The free energy change for a reaction is – 86.5 kJ per mole at 298 K and – 83.50 kJ per mole at 308 K. Calculate the enthalpy change (ΔH) for the reaction at 303 K.

[Ans = – 175.9 kJ]

2. Calculate ΔA and ΔG for the reversible compression of one mole of an ideal gas from 2 atm to 100 atm at 30.2 °C. [Ans ΔA = 2357.25 cal; ΔG = 2357.25 cal]

(a) **For linear molecules of *n* atoms**

Total degrees of freedom = $3n$

Translational degree of freedom = 3

Rotational degree of freedom = 2

∴ Vibrational degree of freedom = $3n - 3 - 2 = 3n - 5$

∴ Number of fundamental bands for a linear molecule = $3n - 5$.

Rotation about the axis of linearity does not bring about any change in the position of atoms while rotation about the other two axes, changes the position of the atoms. Hence, linear molecule has two degrees of rotation.

(b) **For non-linear molecules of *n* atoms**

Total degrees of freedom = $3n$

Translational degree of freedom = 3

Rotational degree of freedom = 3

Vibrational degree of freedom = $3n - 3 - 3 = 3n - 6$

Hence, number of fundamental bands = $3n - 6$

Combination bands and Fermi resonance

Combination bands, difference bands or overtones are produced due to the interaction of the vibrational states in polyatomic molecules. If there are two fundamental bands at a and b, then the additional bands that can be expected are

(i) 2a, 2b (overtones)

(ii) a + b, a + 2b, 2a + b, etc. (combination bands)

(iii) a – b, a – 2b, 2a – b, etc. (difference bands)

The intensity of these bands is 10–100 times less than the intensity of the fundamental bands. When an overtone or combination band falls near the fundamental band, there is resonance and the molecule transfers its energy from the fundamental to the overtone band and back. Due to this resonance, both the bands share their intensity and appear as a pair of equally intense bands in the IR spectrum. Such type of resonance is known as *fermi resonance.*

Solved Examples

(i) Calculate the theoretical number of vibrational degrees of freedom in

(a) Carbon dioxide (b) Benzene

(c) Water (d) Sulphur dioxide (e) N_2O

Solution

(a) CO_2 is a linear triatomic molecule

Vibrational degree of freedom = $3n - 5$ where $n = 3$

$$= 3 \times 3 - 5 = 4$$

(b) C_6H_6 is a non-linear molecule where $n = 12$ (6C + 6H)

Vibrational degree of freedom = $3n - 6$

$$= 3 \times 12 - 6 = 30$$

30 fundamental bands are expected in benzene but the number is less as the bands may fall outside the region under investigation or may be too weak to be observed as bands.

(c) H_2O is a non-linear molecule with $n = 3$

Vibrational degree of freedom = $3 \times 3 - 6 = 3$

Vibrational degree of freedom = $3n - 6$

$$= 3 \times 12 - 6 = 30$$

30 fundamental bands are expected in benzene but the number is less as the bands may fall outside the region under investigation or may be too weak to be observed as bands.

(c) H_2O is a non-linear molecule with $n = 3$

Vibrational degree of freedom = $3 \times 3 - 6 = 3$

(d) SO_2 is a non-linear molecule with $n = 3$

Vibrational degree of freedom = $3n - 6$

$$= 3 \times 3 - 6 = 3$$

(e) N_2O is a non-linear molecule with $n = 3$

Vibrational degree of freedom = $3n - 6$

$$= 3 \times 3 - 6 = 3$$

Practice Problems

(i) Calculate the theoretical number of vibrational degrees of freedom in

(a) HCN (b) $C_6H_5CH_3$ (c) CH_4 [Ans (a) 4 (b) 39 (c) 9]

Solved Example

1. For CO molecule the rotational spectral lines appear at 3.8424 cm^{-1} for the transition J = 0 to J = 1. Calculate the moment of inertia and bond distance for the molecule.

Solution

We know that

$$\bar{\upsilon}_{J\to(J+1)} = \bar{\upsilon}_{0\to1} = 2B$$

Therefore 2B = 3.8424 cm^{-1}

or B = 1.9212 cm^{-1}

Moment of inertial I:

$$I = \frac{h}{8\pi^2 Bc} = \frac{6.624\times10^{-27}}{8\times3.14\times3.14\times1.9212\times3\times10^{10}}$$

$$I = 1.4567\times10^{-39}\ \text{g cm}^2$$

$$= 1.4567\times10^{-46}\ \text{kg m}^2$$

reduced mass of CO ,

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{\dfrac{12}{N_A}\times\dfrac{16}{N_A}}{\dfrac{12}{N_A}+\dfrac{16}{N_A}} = \frac{12\times16}{N_A(12+16)}$$

where N_A = Avogadros number

$$\mu = \frac{12\times16}{6.023\times10^{23}\times28} = 1.14\times10^{-23}\,\text{g mol}^{-1} = 1.14\times10^{-26}\,\text{kg mol}^{-1}$$

$$\text{I} = \mu r^2 \text{ or } r = \sqrt{\frac{I}{\mu}}$$

$$\text{Bond distance } r = \sqrt{\frac{1.4567\times10^{-46}}{1.14\times10^{-26}}} = 1.13\times10^{-8}\,\text{cm}$$

$$= 1.13\times10^{-10}\,\text{m} = 1.131\,\text{A}^\circ = 113\,\text{pm}$$

2. The internuclear distance (bond length) of carbon monoxide molecule is 1.13 Å. Calculate the energy (in joules and eV) of this molecule in the first excited rotational level. Also calculate the angular velocity of the molecule. Given atomic masses of $^{12}C = 1.99\times10^{-26}$ kg; $^{16}O = 2.66\times10^{-26}$ kg.

Solution

$$r = 1.13\ \text{A}^\circ = 1.13\times10^{-10}\ \text{m}$$

$$\mu = \frac{m_1 m_2}{m_1+m_2} = \frac{1.99\times10^{-26}\ \text{kg}\times2.66\times10^{-26}\ \text{kg}}{1.99\times10^{-26}\ \text{kg}+2.66\times10^{-26}\ \text{kg}} = 1.14\times10^{-26}\ \text{kg}$$

moment of inertia $I = \mu r^2$

$$I = 1.14\times10^{-26}\ \text{kg}\times(1.13\times10^{-10}\ \text{m})^2 = 1.46\times10^{-46}\ \text{kg m}^2$$

$$\mu = \frac{m_1 m_2}{m_1 + m_2} = \frac{1.99 \times 10^{-26}\ \text{kg} \times 2.66 \times 10^{-26}\ \text{kg}}{1.99 \times 10^{-26}\ \text{kg} + 2.66 \times 10^{-26}\ \text{kg}} = 1.14 \times 10^{-26}\ \text{kg}$$

moment of inertia $I = \mu r^2$

$$I = 1.14 \times 10^{-26}\ \text{kg} \times (1.13 \times 10^{-10}\ \text{m})^2 = 1.46 \times 10^{-46}\ \text{kg m}^2$$

Energy of a rigid diatomic molecule is given by

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1)\ \text{Joule}$$

For the first excited level, J=1; hence

$$E_1 = \frac{(6.626 \times 10^{-34})^2 \times 1(1+1)}{8 \times 3.14 \times 3.14 \times 1.46 \times 10^{-46}\ \text{kg m}^2}$$

$$= 7.61 \times 10^{-23}\ \text{Joule}$$

since $1\ \text{eV} = 1.602 \times 10^{-19}\ \text{J}$

$$E_1 = \frac{7.61 \times 10^{-23}}{1.602 \times 10^{-19}\ \text{J eV}^{-1}}$$

$$= 4.76 \times 10^{-4}\ \text{eV}$$

$$\text{angular velocity } \omega = \sqrt{\frac{2E_1}{I}} = \sqrt{\frac{2 \times 7.61 \times 10^{-23}\ \text{J}}{1.46 \times 10^{-46}\ \text{kg m}^2}} = 3.32 \times 10^{11}\ \text{radians}^{-1}$$

Practice Problems:

1. The pure rotational (microwave) spectrum of gaseous HCl consist of a series of equally spaced lines separated by 20.80 cm^{-1}. Calculate the bond distance of the molecule. The atomic masses are $^{1}H = 1.673 \times 10^{-27}$ kg; $^{35}Cl = 58.06 \times 10^{-27}$ kg [Ans 129 pm]

2 For a rigid diatomic molecule the rotational constant at 300 K is 1.566 cm^{-1}, calculate the value of J$_{max}$. [Ans 7.56 ≈ 8]