Eastern University, Sri Lanka

Special degree Examination in Chemistry -2011/2012 (November 2015)

CHS 03 Physical Chemistry -I

Answer all questions

Time: 02 hours

1. (a) Define the terms thermal expansion coefficient (α) and isothermal compressibility (

Derive the first thermodynamic equation of state $\left(\frac{\partial U}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V - P$ from the Auxilia

equation $dU = TdS - PdV$ and Maxwell's relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$.

Hence show that

i) $\left(\frac{\partial P}{\partial T}\right)_V = \frac{\alpha}{\beta}$

ii) the difference in the heat capacities $C_p - C_V = \frac{\alpha^2}{\beta} TV$.

iii) calculate α and β for a gas that obeys the equation of state $P(V - b) = RT$.

(60 mark

(b) At constant temperature the variation of fugacity with pressure is given by equation:

$$\frac{\partial \ln f}{\partial p} = \frac{V_m}{RT}$$

Derive an expression for the fugacity of a gas that obeys the equation of state

$$pV_m = RT + a_1 p + a_2 p^2$$

For a particular gas $a_1 = 1.502\text{x}10^{-2}$ dm^3 and $a_2 = 4.311\text{x}10^{-4}$ atm^{-1} dm^3
Calculate its fugacity at 298 K and 1 atm.

(40 marks)

2) (a) The Sackur – Tetrode equation for the molar entropy of a perfect mono[atomic gas]
could be written in the form of $S_m = R\ln\left(\frac{aT^{5/2}}{p}\right)$ where a is a com[bination of]
constants.

i) Show that the combination of constants of $a = \frac{(ek)^{5/2}(2\pi m)^{3/2}}{h^3}$ and e[xplain the]
terms involved in this expression.

ii) From the Auxiliary equation $dG = VdP - SdT$, show that the chan[ge in molar]
Gibbs energy when heating the sample from T_1 to T_2 at constant press[ure is]

$$\Delta G_m = R\ln\left(\frac{a}{p}\right)[T_1 - T_2] - \frac{5R}{2}\int_{T_1}^{T_2}\ln T\, dT$$

iii) Evaluate the change in molar Gibbs energy that accompanies heatin[g the]
sample from 273 K to 373 K at constant pressure ($\frac{a}{p} = 79.82$)

[Use $\int \ln x\, dx = x\ln x - x$]

(7...

(b) Calculate the ratio of the translational partition functions of D_2 and H_2 ...
at the same temperature and volume.

(3...

3) (a) i) Write the Hamiltonian for a real system in terms of first order Per[turbation]
theory.

ii) Show that the average energy of the system is given by,

$$< E > = < E^{(0)} > + < E^{(1)} >$$

Where $< E^{(0)} >$ = Average energy of the ideal system = $\int (\psi^{(0)})^* \hat{H}$...

$< E^{(1)} >$ = First order correction to the energy = $\int (\psi^{(0)})^* \hat{H}^{(1)}$...

iii) A particle of mass m is in a box having length a. The potential energ[y]
is given by the function $V = kx^2$. Using the Perturbation theory a[nd the wave]
function inside box as $\psi = \sqrt{\frac{2}{a}}\sin\left(\frac{\pi x}{a}\right)$

show that the average energy of the particle inside the box is,

$$< E > = \frac{h^2}{8ma^2} + \frac{ka^2}{3}$$

[Use $\int x^2 sin^2\, bx\, dx = \frac{x^3}{6} - \left(\frac{x^2}{4b} - \frac{1}{8b^3}\right)\sin(2bx) - \frac{x}{4b^2}\cos(2bx)$ and ...

(8...

(b) Construct a proper antisymmetric wave function for Be in terms of a Slater determina

(20 mark

(a) The first electronically excited state of the O_2 molecule is 1_{Δ_g} (doubly degenerate) a
lies 7918 cm[-1] above the ground state, which is 1_{Σ_g} (triply degenerate).

Derive the following equations for internal energy (E) and entropy (S) using the conc in statistical thermodynamics,

i) $E = NKT^2 \frac{1}{q}\left(\frac{\partial q}{\partial T}\right)_V$

ii) $S = NK[\ln q + T\left(\frac{\partial \ln q}{\partial T}\right)_V]$

iii) Calculate the electronic contribution to the molar internal energy (E) and molar Helmholtz free energy (A) of the O_2 molecule at 400 K.

(70 mark

(b) Calculate the Huckel Molecular Orbital energies of the planer radical CH_2CHC and show that the π electronic energy $E_\pi = 3\alpha + 2\sqrt{2}\beta$.

(30 marks

@@@@@@@