(1)At 25 °C the enthalpy of the graphite --> diamond phase transition is 1.896 KJ/mol, and the entropy is -3.2552 J/K mol. (a)What's the spontaneous direction at 25 °C? (b)Which direction is favored by a rise of temperature? (6%)

(2)At 90 °C the vapor pressure of toluene is 400 mmHg, and that of o-xylene is 150 mmHg. (a)What's the composition of a liguid mixture that will boil at 90 °C when the pressure is 0.5 atm? (b)What's the composition of the vapor produced? (6%)

(3)The standard e.m.f. of the cell

$$Pt\ |\ H_2(g)\ |\ HCl(aq.)\ |\ Hg_2Cl_2(s)\ |\ Hg(l)$$

was found to be 0.2699 V at 293 °K and 0.2669 V at 303 °K. Evaluate the ΔG°, ΔH° and ΔS° of the reaction at 298 °K. (6%)

(4)A piston exerting a pressure of 1 atm rests on the surface of water at 100 °C. The pressure is reduced infinitesimally, and as a result 10 g of water evaporate. This process absorbs 22.2 KJ of heat. What are the values of q, w, ΔU and ΔH. (Atomic weight: H=1, O=16) (8%)

(5)(a)C_p for an ideal gas is given by $C_p=a+bT$ for the reversible adiabatic expansion of this gas, show that $R\ \ln(V_1/V_2) = (a-R)\ln(T_2/T_1) + b(T_2-T_1)$.
(b)For N_2 gas, $a=27.3\ JK^{-1}mol^{-1}$, $b=5.2\times10^{-3}\ JK^{-2}mol^{-1}$, calculate the temperature resulting the reversible adiabatic compression of nitrogen from a volume of 10 liters to a volume of 1 liter, the initial temperature being 25 °C. (8%)

(6)The wave function for a hydrogenlike atom in the 1S state is found to be

$$\Psi = \pi^{-1/2}(Z/a_o)^{3/2}e^{-Zr/a_o}$$

Calculate the expectation value of r. (9%)

(7)Given that $\hat{L}_x = i\hbar\{\sin\phi\ (\partial/\partial\theta) + \cot\theta\ \cos\phi\ (\partial/\partial\phi)\}$ and $\hat{L}_z = -i\hbar\partial/\partial\phi$, calculate $[\hat{L}_x, \hat{L}_z]$. Does $\hat{L}_x$ and $\hat{L}_z$ commute with each other? (8%)

(8)Write down the complete wave functions for an excited He atom described as 1S(1)2S(2). Be sure to include all possible wave functions. (8%)

(9)According to the Boltzmann distribution law, the fraction f_n of the molecules in the n-th energy state ε_n is given by

$$f_n = \exp(-\varepsilon_n/kT)/\sum_n \exp(-\varepsilon_n/kT)$$

For a harmonic oscillator having frequency $k\theta/h$, what's the overall probability that the oscillator is in its excited states. ($n \geq 1$) (8%)

(10)Given the distribution function for the translational energy of gas molecules $dN/N = 2\pi(\pi kT)^{-3/2}\ \varepsilon_{tr}^{1/2}\exp(-\varepsilon_{tr}/kT)\ d\varepsilon_{tr}$, find the most probable molecular translation energy ε_{mp} for an ideal gas. (5%)

(11)For the following reversible first-order reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} Z$, if initially only A is present, (a)Write the rate equation for d[A]/dt. (4%)
(b)Integrate the rate equation in (a). (6%)
(c)Derive the relation between the relaxation time and the rate constant for this reaction which is subjected to a small displacement from equilibrium. (4%)

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(12)For the mechanism (1) $A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C + D$; (2) $2C \xrightarrow{k_2} G + H$, step 2 is rate-determining. Given the activation energies $E_{a,1}$=30 Kcal/mol, $E_{a,-1}$=24 Kcal/mol, and $E_{a,2}$=49 Kcal/mol for k_1, k_{-1}, and k_2, respectively.

(a)Derive the rate law for this reaction. (5%)

(b)Calculate E_a for the overall reaction. (4%)

(13)CsBr has the simple cubic structure. Its density at 20 °C is 4.44 g/cm^3. Calculate the unit-cell length and the nearest-neighbor distance in CsBr. (M. Wt. of CsBr= 212.8 g/mol). (5%)