1. One mole of benzene is mixed with five moles of toluene. At 60°C the vapor pressure of benzene and toluene are 51.3 and 18.5 KPa, respectively. (a) As the pressure is reduced, at what pressure will boiling begin? (b) what will be the composition of the first bubble of vapor? (6%)

2. For the reaction $(CH_3)_2CHOH(g) = (CH_3)_2CO(g) + H_2(g)$ $K_p = 0.45$ at 452 K. Calculate: (a) ΔG° and (b) ΔG when the pressure of $(CH_3)_2CHOH$ is maintained at 1 bar, $(CH_3)_2CO$ and H_2 are removed at a partial pressure 0.01 and 0.02 bar, respectively. (c) Is the reaction spontaneous under the later condition? (8%)

3. A reversible cycle can be completed in three steps. such as: isothermal expansion (at T_2) from V_1 to V_2, cooling (at constant V_2) from T_2 to T_1, and adiabatic compression back to the initia state. (a) Draw a diagram of this cycle using T and V as coordinates. (b) A nonideal gas that obeying $PV = RT + BP$ (B = constant) is carried through this cycle, compute ΔS for each step and (c) show that $\oint dS = 0$ for this cycle. Assume C_V is constant. (10%)

4. (a) Show that $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ (3%)
(b) calculate that $\left(\frac{\partial U}{\partial V}\right)_T$ for a perfect gas, $PV = RT$ (3%)
(c) Calculate $\left(\frac{\partial U}{\partial V}\right)_T$ for a real gas that obeying van der Waals' equation $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ (4%)

5. For the hydrogen atom if the masses of the electron and nucleus are m and M, a) find its reduced mass μ; b) find its moment of inertia I; c) what happen to μ and I when $M \to \infty$. (8%)

6. a) Write the Schrödinger equations of the electronic and nuclear wave-functions ψ_{el} and ψ_{nu} for the molecule H_2^+ in Born-Oppenheimer (BO) approximation; b) write the corresponding Hamiltonians $\hat{H}_{el}$ and $\hat{H}_{nu}$; c) give the definition and draw the diagram of the potential energy cure (15%)

7. Draw the energy levels for a rigid rotator and indicate their: a) energy values. b) degeneracies. c) the selection rules for the

036

rotational spectra; d) the wave number $\tilde{\nu}$ resulting from the given transitions. (11%)

8. Given the probability density function for v_x of gas molecules with molecular mass m, $f(v_x)=\left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} \exp(-mv_x^2/2kT)$, derive a) the most probable speed, v_{xp} (4%)
   b) the average of v_x^2, $\langle v_x^2 \rangle$ (6%)
   for v_x at temperature T.

9. Prove that $(k_1k_4+k_1k_5+k_4k_6)/(k_2k_4+k_2k_5+k_3k_5)=k_1/k_2$ if $k_1k_3k_5=k_2k_4k_6$. (5%)

10. If the rate constant of a chemical reaction follows $k=aT^m \exp(-E_0/RT)$, where a and m are constants and E_0 is a hypothetical activation energy at 0 K. Derive an expression for the Arrhenius activation energy E_a in terms of E_0 (6%)

11. Lithium forms body-centered cubic crystals. The length of each side of the unit cell is 0.351 nm. Calculate the radius of a Lithium atom. (6%)

12. What is the root-mean-square displacement in the x direction of a myoglobin molecule due to its Brownian motion in one minute in water at 20°C ? The diffusion coefficient of the myoglobin molecules at 20°C is $D=1.24\times10^{-10}\ m^2\ s^{-1}$. (5%)