國立中山大學100學年度碩士班招生考試試題
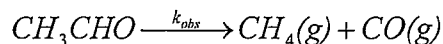
科目：物理化學【材光系碩士班甲組】
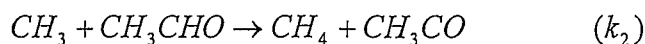
1. Given the van der Waals constants for ethane gas as $a = 5.562$ L^2 bar/mol^2, (20%, each 5%)
   $b = 0.06380$ L/mol, for 10.0 mol of ethane at 300 K and under 30 bar,
   where $R = 0.08314$ L-bar/K-mol
   (a) find the second virial coefficient B at this temperature.
   (b) calculate the compressibility factor Z from the first two terms.
   (c) estimate the approximate molar volume from Z.
   (d) what is its Boyle temperature T_B?

2. When 3.0 mol O_2 is heated at a constant pressure of 3.25 atm, its temperature increases from 260 K to 285 K. Given that the molar heat capacity of O_2 at constant pressure is 29.4 J K^{-1} mol^{-1}, calculate q, ΔH, and ΔU. (15%, each 5%)

3. Some polymers can form liquid crystal mesophases with unusual physical properties. For example, liquid crystal Kevlar (as following picture) is strong enough to be the material of choice for bulletproof vests and is stable at temperatures up to 600 K. What molecular interactions contribute to the formation, thermal stability, and mechanical strength of liquid crystal mesophase in Kevlar? (5%)

4. From their atomic numbers and mass numbers, decide whether the following nuclei are likely to have zero, half-integral or integral spin: (a) ^{18}O, (b) ^{10}B, (c) ^{13}C, (d) ^{14}N, (e) ^{19}F (10%, each 2%)

5. The first generally available NMR spectrometer operated at a frequency of 60 MHz; today it is also common to use a spectrometer that operates at 600 MHz. (a) What are the relative population differences of ^{13}C spin states in these two spectrometers at 25 °C (4%)? What are the relative values of the chemical shifts observed for nuclei in these spectrometers in terms of (b) δ value (3%), (c) frequencies (3%)? (10%)

6. Which of the following molecules may show infrared absorption spectrum or Raman spectrum? (a) H_2, (b) HCl, (c) CH_4, (d) CH_3Cl, (e) CH_3CH_3 (10%, each 2%)

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7. Derive the foramtion of CH_4 from the thermal decomposition of acetaldehyde

$$CH_3CHO \xrightarrow{k_{obs}} CH_4(g) + CO(g)$$

A proposed mechanism is

$$CH_3CHO \rightarrow CH_3 + CHO \qquad\qquad (k_1)$$

$$CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO \qquad\qquad (k_2)$$

$$CH_3CO \rightarrow CH_3 + CO \qquad\qquad (k_3)$$

$$2CH_3 \rightarrow C_2H_6 \qquad\qquad (k_4)$$

(10%)

8. The Arrhenius equation $k = A\exp(-E_a / RT)$

   (a) Sketch a plot of $\ln(k)$ as a function of $(1/T)$ and indicate A and E_a, on your graph

   (b) The rate constant for the decomposition of a certain substance is 2.17 L/mols at 840 K and 0.035 at 730 K, Calculate E_a for the reaction

(10%, each 5%)

9. (a) Using the Gibbs - Helmoltz equation $\left[\dfrac{\partial}{\partial T}\left(\dfrac{\Delta G^0}{T}\right)\right] = \dfrac{-\Delta H^0}{T^2}$ to derive Van't Hoff equation

$$\ln K_p = \ln K_p{}^0 - \frac{\Delta H^0}{R}\left(\frac{1}{T} - \frac{1}{T^0}\right)$$

(b) Given that ΔH^0 has an average value of - 69.8 kJ/mol over the temperature range 500 K to 700 K for the reaction described by $PCl_3(g) + Cl_2(g) \Leftrightarrow PCl_5(g)$

Estimate K_p at 700 K given taht $K_p = 0.0408$ at 500 K

(10%, each 5%)