

國立中央大學八十六學年度碩士班研究生入學試題卷

所別: 化學研究所 不分組 科目: 物化、分析 共 2 頁 第 1 頁

物化部份

1. Now we have a heat engine that operates in the following cycle (Note: every step is reversible):

State (a) to state (b) is an isothermal process.

State (b) to state (c) is an adiabatic process.

State (c) to state (d) is an isothermal process.

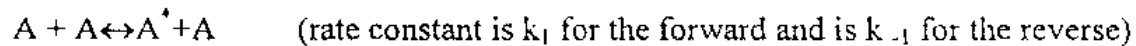
State (d) to state (a) is an isochoric process

If this engine operates on one mole ideal gas and $P_a=4$ atm, $V_a=2$ liter, $P_b=2$ atm, $V_b=4$ liter, $P_d=2$ atm, $V_d=2$ liter, please answer the following questions

- What are the values of P_c , V_c and the two temperatures of the two isothermal curves? (4 points)
- Please write down the values of ΔE (change of energy), q (heat), w (work) of each step (a) \rightarrow (b), (b) \rightarrow (c), (c) \rightarrow (d), (d) \rightarrow (a) (Here, we define $\Delta E = q - w$). (12 points)
- Based upon the above, please show that ΔS (Entropy) of the whole cycle is zero. (2 Points).

2. Liquid helium boils at about 4K and liquid hydrogen boils at about 20K. What is the efficiency of a reversible engine operating between heat reservoirs at these temperatures? (2 points)

3. A unimolecular gas reaction is proposed as



The species A^* is in excited state, present in low concentration. If the steady state approximation is applied here, please show that the mechanism predicts first-order kinetics at higher A concentration and second-order kinetics at lower A concentration. (5 points)

4. In the far-IR spectrum of HBr, there is a series of lines having a separation of 16.94cm^{-1} , Please calculate the moment of inertia and bond length of HBr. (5 points)

5. For a particle in a one-dimensional box (length = L), please show that

$$\Delta p_x \cdot \Delta x = \frac{h}{4\pi} \sqrt{1 + \frac{n^2\pi^2 - 3^2}{3}} > \frac{h}{4\pi}$$

(Hint: $\Psi_n = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$) (10 points).

6. Please write down the electronic configuration and the ground electronic state term symbol of Li (lithium) (4 points)

7. Please write down the molecular orbital (MO) energy diagrams of N_2 and O_2 (6 points)

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分析部份

1. Describe briefly the principle of Fourier Transform IR (FT-IR) Spectroscopy and what are the advantages of FT-IR spectroscopy compared with a Dispersive instrument? (10 points)
2. What are the principle, advantages and limitations of each of the following detectors used in gas chromatography: (a) thermal conductivity (b) atom emission (c) electron capture and (d) flame ionization detectors. (10 points)
3. Try to define the following terms: (10 points)
 - (a) Coherent radiation
 - (b) photoelectric effect
 - (c) fluorescence
 - (d) phosphorescence
4. From the standpoint of Boltzmann distribution explain why increasing flame temperature enhance the sensitivity of AES more than it does to AAS. (10 points)
5. In oxidation/reduction titration, why the change in E_{system} in the equivalence point region is controlled by the difference between $E^{\circ}_{\text{reductant}}$ and $E^{\circ}_{\text{oxidant}}$. How does this difference relate to K_{eq} (equilibrium constant)? (10 points)