國 立 清 華 大 學 命 題 紙

八十六學年度 化學工程學系 系（所） 乙 組碩士班研究生入學考試

科目 物理化學 科號 1701 共 2 頁第 1 頁 *請在試卷【答案卷】內作答

Problem 1 (20%)

One mole of an ideal gas of C_v=5.0 cal/mole-deg initially at standard temperature and pressure is put through the following reversible cycle (A:) State 1 to state 2, heated at constant volume to twice the initial temperature. (B:) State 2 to state 3, expanded adiabatically until it is back to the initial temperature. (C:) State 3 to State 1, compressed isothermally back to state 1. Calculate q, w, ΔE and ΔH for steps A and B and for the cycle.

Problem 2 (20%)

For each of the cases that follow list as many properties of the equilibrium state as you can, especially the constraints placed on the equilibrium state of the system by its surroundings and/or its container.

(a) The system is placed in thermal contact with a thermostatic bath maintained at the temperature T.

(b) The system is contained in a constant-volume container and thermally and mechanically isolated from its surroundings.

(c) The system is contained in a frictionless piston and cylinder exposed to an atmosphere at pressure P and thermally isolated from its surroundings.

(d) The system is contained in a frictionless piston and cylinder exposed to an atmosphere at pressure P and is in thermal contact with a thermostatic bath maintained at the temperature T.

(e) The system consists of two tanks of gas connected by tubing. A valve between the two tanks is fully opened for a short time and then closed.

Problem 3 (20%)

(a) How many degrees of freedom has a system containing only water which is at the triple point?

(b) How many degrees of freedom has a system containing liquid water and liquid benzene in equilibrium with their vapors?

(c) What is the virial equation state? When does one use the virial equation?

(d) Using the definition of enthalpy, H=U+PV, show that $C_p = C_v + R$ for an ideal gas.

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Problem 4 (20%)

解釋下列名詞:(八題選五題回答、每題4分,共20分,每題約用50字回答,不必翻譯名稱。)

a) exclusion principle (Pauli's)

b) UV photoelectron spectroscopy

c) Born-Oppenheimer principle

d) Franck-Condon principle

e) zero-point energy

f) de Broglie relation

g) LCAO-MO

h) Walsh diagram

Problem 5 (20%)

I. For a bi-atomic combination reaction of $B + C \xrightarrow{k} D$.

a). What is the relationship of the pre-exponential factor (A) of the rate constant k with the diameter (d) and mass (m) of atoms B and C according to the collision theory? 5%

b) What is the unit of A? 5%

II. a). How many degrees of freedom in translation, vibration and rotation, does a linear molecule composed of N atoms have ? 6%

b) According to the activated complex theory, the rate constant k of an elementary reaction $B + C \xrightarrow{k_c} D$ should be $k_c = \nu K$, what are the physical meaning of the ν and the K? 4%