八十六學年度材料科學工程研究所(系)(所) 第三 組碩士班研究生入學考試

科目 物理化學(I) 科號 2201 共 3 頁第 1 頁 *請在試卷【答案卷】內作答

1. 15%

The van der Wall equation of state correct the ideal gas law PV=RT (for 1 mole of gas) for real gas.

(a) What is the van der Wall equation of state?

(b) What approximations do we make for the ideal gas model?

(c) How do your equation in (a) correct the approximations in (b)?

(d) The van der Wall equation of state can be expanded with the virial coefficients of state:

$$P = \frac{RT}{V}\left(1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots\right)$$

Derive B and C.

2. 5%

The entropy is the basic term of statistical mechanics.

(a) What is the Boltzmann definition of entropy in terms of probability? Define each term clearly.

(b) What does the entropy change when one mole of gas with volume V freely expand to 2V?

3. 20%

The partition function is the prime tool in statistical mechanics.

(a) How do you define a partition function?

(b) What is the total partition function of one mole of a diatomic molecule in terms of partition functions of translation, internal motion, electronic states and nuclear states.

(c) Use the particle in a box model to derive the translational partition function.

(d) If the electronic ground state is a triplet state, what is the electronic partition function?

(e) What is the vibrational partition function if the vibrational frequency is υ for this diatomic molecule?

4. How does the partition function of the preceding problem affect the heat capacity of an ideal diatomic gas? (5%)

5. Consider the heat capacity of solids. (5%)
   (a) What is the law of Dulong and Petit? What is its restriction?
   (b) How does Einstein's theory correct to release the restriction in (a)?
   (c) How does Debye's theory further correct Einstein's theory?

6. Use the steady-state approximation to solve [A] (t), [B](t) and the differential rate equation of reaction interms of A_0 and B_0

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} AB \xrightarrow{k_2} C + A$$

given the initial concentration of A and B to be A_0 and B_0, respectively, and [A] is in excess. (10%)

7. Estimate the order of magnitude for the collision frequency (per second) of a N_2 molecule at 300 K under 1 atm of pressure. (5%)

8. When the potential of intermolecular interaction is best described to be $\propto \frac{1}{R^6}$, whereas R denotes the intermolecular distance. What kind of force is used to describe this interaction? (Write down the name of the force) (4%).
   Which following set of molecules below the interparticle interaction is best described to be $\propto \frac{1}{R^6}$ (a) He – He (b) $Cs^+ - Cl^-$ (c) Na^+–Cl (d) HF–H_2O. (3%)

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科目 物理化學(I) 科號 2201 3301 共 2 頁第 3 頁 *請在試卷【答案卷】內作答

9. The reaction $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$ can be activated by UV light. One assumes that the photon intensity measured before the reaction cell is I_o and after the cell is I and the absorption follows Beer-Lambert law. After several experimental measurements, we determine the differential rate equation for this reaction to be $\frac{d[HBr]}{dt} = \frac{a[H_2][Br_2](I_o - I)}{[Br_2] + b[HBr]}$, in which a and b are the rate coefficiencies. Derive a mechanism to elaborate these results. (12%)

10. Label each of the following statements as either true or false. If a statement is true only under special circumstances, label it as false. (6%)
    (a) The mean molecular kinetic energy of a gas is independent of the molecular mass.
    (b) The order of a reaction with respect to a substance is not necessarily equal to the stoichiometric coefficient of that substance in the reaction equation.
    (c) First-order processes occur only in chemical processes.

11. For a simple two-body collision, the potential energy of interaction of particles is V(r), and the initial relative kinetic energy is E_o. If the impact parameter for the collision is b, calculate the distance of closest approach of these two particles. (10%)