

八十六學年度材料科學工程研究所(系) 三 組碩士班研究生入學考試

科目 物理化學(I) 科號 220/330 共 3 頁第 1 頁 \*請在試卷【答案卷】內作答

1. 15%

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

- What is the van der Waal equation of state?
- What approximations do we make for the ideal gas model?
- How do your equation in (a) correct the approximations in (b)?
- The van der Waal equation of state can be expanded with the virial coefficients of state:

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

Derive  $B$  and  $C$ .

2. 5%

The entropy is the basic term of statistical mechanics.

- What is the Boltzmann definition of entropy in terms of probability? Define each term clearly.
- What does the entropy change when one mole of gas with volume  $V$  freely expand to  $2V$ ?

3. 20%

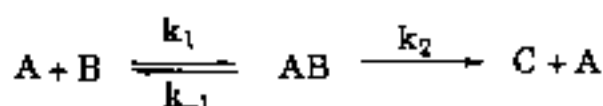
The partition function is the prime tool in statistical mechanics.

- How do you define a partition function?
- 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.
- Use the particle in a box model to derive the translational partition function.

八十六學年度材料科學工程研究所(系) 2201 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 2 頁 \*請在試卷【答案卷】內作答

- (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  $\nu$  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 in terms of  $A_0$  and  $B_0$



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)  $Ca^+ - Cl^-$  (c)  $Na^+ - Cl$  (d) HF -  $H_2O$ . (3%)

八十六學年度材科學工研研究所(系)(所)  $\Psi \Sigma$  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 3 頁 \*請在試卷【答案卷】內作答

9. The reaction  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$  can be activated by UV light. One assumes that the photon intensity measured before the reaction cell is  $I_0$  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  $\frac{d[\text{HBr}]}{dt} = \frac{a[\text{H}_2][\text{Br}_2](I_0 - I)}{[\text{Br}_2] + b[\text{HBr}]}$ , in which  $a$  and  $b$  are the rate coefficients. 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%)
- The mean molecular kinetic energy of a gas is independent of the molecular mass.
  - 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.
  - 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  $E_0$ . If the impact parameter for the collision is  $b$ , calculate the distance of closest approach of these two particles. (10%)