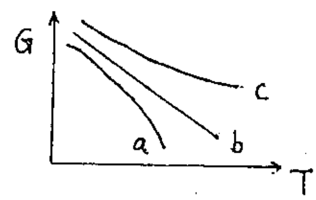
國立中山大學九十二學年度博士班招生考試試題

科目：材料科學【材料所甲組】

Answer any 10 of the following 15 questions.

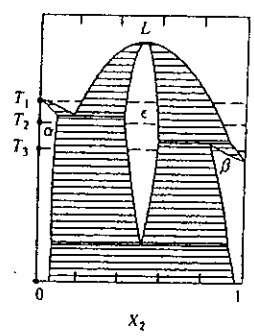
1. Derive the following equations:
   $(\partial G/\partial P)_T = V$
   $(\partial G/\partial T)_P = -S$
   $(\partial (G/T)/\partial (1/T))_P = H$ (10%)

2. The temperature dependence of Gibbs free energy of an element in solid state is shown schematically in the figure. Determine which curve is correct and explain why. (10%)



3. Determine the maximum pressure of water vapor in wet hydrogen at 1 atm pressure in which chromium can be heated without oxidation occurring at 1500 K. Is the oxidation of Cr by water vapor exothermic or endothermic?
   k = 8.314 J/mole K.
   $2\ Cr_{(s)} + 3/2\ O_{2(g)} = Cr_2O_{3(s)}$ $\Delta G^\circ = -1120300 + 260\ T$ Joules
   $H_{2(g)} + 1/2\ O_{2(g)} = H_2O_{(g)}$ $\Delta G^\circ = -246000 + 54.8\ T$ Joules (10%)

4. Plot the free energy-composition diagrams at T_1, T_2 and T_3 that correspond to the phase diagram with an intermediate phase, as shown in the figure. (10%)



5. The $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ position in the fcc structure is a tetrahedral site, an interstice with fourfold atomic coordination. How many tetrahedral sites are there per fcc unit cell? (10%)

6. List the members of the {100} family of planes in (a) the cubic system and (b) the tetragonal system. (10%)

7. An aluminum single crystal is oriented so that a tensile load is applied along the [001] crystal direction. If the applied stress is 10 MPa, what will be the resolved shear stress, τ, along the $[10\bar{1}]$ direction within the (111) plane. (10%)

8. Why is there no base-centered cubic lattice in the fourteen crystal (Bravais) lattices? (10%)

9. A crystal of BCC structure is examined by x-ray diffraction, and several Bragg diffraction peaks are observed. It is known that for BCC structure, the Bragg diffraction occurs when h+k+l = even number, where h, k, and l are Miller indices to characterize crystal plane. What will be the ratio of the interplanar spacings corresponding to the first three diffraction peaks? (10%)

10. The initial sintering rate for BaTiO3 increases 10 times by raising the temperature from 750 to 794℃. Predict the temperature at which the initial sintering rate would have increased 100 times compared to 750℃. (10%)

11. Explain why ice melts at 0°C, but water solidifies/crystallizes at temperatures slightly lower than 0°C. (10%)

12. Explain the following terms: (a) condensed matter, (b) crystal, (c) glass, (d) supercooled liquid, (e) nanophase effect. (10%)

13. In brittle materials the larger the specimen, the lower the fracture strength. Why? (10%)

14. Use the free energy-composition diagram to describe the conditions for spinodal decomposition, and tell the difference between spinodal decomposition and nucleation and growth transformation. (10%)

15. Describe the strengthening mechanisms normally involved in strengthening engineering alloys. (10%)

Please note there are three parts and altogether 12 questions in this examination. Be sure to give your answer according to the number of the question (beware the alphabetical number and symbol we use to number the question).

Part A. 高分子合成與反應 (30%)

(1) Polyester can be prepared from polycondensation reaction between difunctional monomers (e.g. both hydroxyls of a diol). Suppose that a polycondensation was performed between a aliphatic diol ($HO\text{-}(CH_2)_n\text{-}OH$, a A-A monomer) and a dicarbonyl compound ($XOC\text{-}(CH_2)_m\text{-}COX$, a B-B monomer) according to the following equation:

$$HO-(CH_2)_n-OH + XOC-(CH_2)_m-COX \xrightarrow{k} \left[OCO\text{-}(CH_2)_m\text{-}CO\text{-}O-(CH_2)_n \right]_x + HX$$

X = -OH, -OR, -Cl

Where, k is the rate constant of the polycondensation.

(a) Here, polyester can be prepared from reaction of a diol (A-A) with dicarboxylic acid (B-B, in which X = -OH), diester (X = OR) or diacyl chloride (X = Cl). Which of the starting monomers will yield a highest rate for polymerization? (5%) Why? (5%)

(b) To simplify the kinetics for polycondensation, *the principle of equal reactivity* is generally applied to approach the reactivity of the functional groups of a bifunctional monomer. Generally, we can express the polymerization rate in term of $-d[A\text{-}A]/dt = k[A\text{-}A][B\text{-}B]$.

i) Specify which of the variables ($-d[A\text{-}A]/dt$, k, [A-A] or [B-B]) in the above rate expression is directly related to the reactivity mentioned above. (5%)

ii) Does the reactivity change with the polymerization temperature? (3%) Give your reason. (5%)

(c) To facilitate the polycondensation between diol and diacyl chloride (B-B, in which X = Cl), a weak base (e.g. triethylamine or pyridine) was generally added during the polymerization. Specify the function of the weak base applied here. (7 %)

Part B. 高分子物性 (40%)

(2) Size exclusion chromatography (SEC) is used to determine the molar mass distribution of polymers. SEC is not an absolute method. It requires calibration. Narrow molar mass fractions of atactic polystyrene are commonly used for calibration. The time for a given molecular species to flow through the column is dependent on the hydrodynamic volume of the molecule. It has been shown that the hydrodynamic volume is proportional to the product of the intrinsic viscosity $[\eta]$ and the molar mass M. The Mark-Houwink equation relates the two quantities according to: $[\eta] = KM^a$

where K and a are constants unique for a given combination of polymer, solvent and temperature. Suggest a simple laboratory experiment that can be used to determine the constants in this equation. (5%)

Derive the relationship between the molar masses of the polymer studied and of atactic polystyrene for a given elution time. (5%)

(3) Define the following terms: healing of the polymer, conformation, polymer single crystal, specific viscosity, θ-solvent. (10%)

(4) The crystallization rate of isotactic polypropylene (M_w = 181,000, T_m = 172°C) was studied under various patterns of temperature change. Solids were melted at T_f, held at T_f for 1 hr, and then crystallized at T_c. The following Avrami exponents (n) were observed.

	Avrami exponent		
T_f(°C)	T_c = 150°C	T_c = 155°C	T_c = 160°C
190	-	3.1	3.5
210	2.9	3.3	4.1
220	3.1	3.8	-
230	3.1	4.0	-

On the basis of these observations, criticize or defend the following propositions:

(a) When both T_f and T_c are low, the Avrami exponents are consistent with three dimensional growth on contact with sporadic nucleation. (5%)

(b) The change in n can be interpreted as arising from a change in either the growth geometry or nucleation situation. That is, the change in n for [T_f and T_c low] → [T_f and T_c high] could arise from either the change spherical → disk geometry or the change sporadic → simultaneous nucleation. (5%)

(5) List the general factors of chemical structure that affect T_g. Discuss the effect of copolymerization on T_g. (10%)

Part C. 高分子加工 (30%)

(6) Show that the *equation of continuity*, which is typically written as

$$\partial\rho/\partial t = -(\vec{\nabla} \bullet \rho\vec{v}) \quad \text{(C1)}$$

(in which t, ρ, and v are respectively the time, the density, and the velocity of the fluid and the arrows are used to emphasize vectors) can be expressed as

$$D\rho/Dt = -\rho(\vec{\nabla} \bullet \vec{v}), \quad \text{(C2)}$$

if an operator, the 'substantial derivative' defined as $D/Dt = \partial/\partial t + \vec{v} \bullet \vec{\nabla}$, (C3)

is adopted. [3%]

(7) Similarly, show that the *equation of motion*, typically written as

$$\partial[\rho\vec{v}]/\partial t = -[\vec{\nabla} \bullet \rho\vec{v}\vec{v}] - [\vec{\nabla} \bullet \underline{\underline{\pi}}] + \rho\vec{g} \quad \text{(C4)}$$

can be expressed as $\rho[D\vec{v}/Dt] = -[\vec{\nabla} \bullet \underline{\underline{\pi}}] + \rho\vec{g}$ (C5)

(in which g represents gravity and the stress tensor $\underline{\underline{\pi}} = P\underline{\underline{\delta}} + \underline{\underline{\tau}}$, (C6)

with P, δ, and τ represent respectively the pressure, the unit (identity) tensor, and the deviatoric stress tensor whereas double-underlines are used to emphasize tensors). [3%]

(8) What is the physical meaning of the *equation of continuity*? [3%]

(9) What is the physical meaning of the *equation of motion*? [3%]

(10) What is the physical meaning of the *substantial derivative*? [3%]

(11) On the basis of Equation C5, Equation C6 can be rewritten as

$$\rho[D\vec{v}/Dt] = -\vec{\nabla}P - [\vec{\nabla} \bullet \underline{\underline{\tau}}] + \rho\vec{g}\,. \qquad \text{(C7)}$$

Regarding the pressurization of polymer melt during polymer processing (which is an important operation in the molding or extrusion of polymers), what approaches does Equation C7 suggest? Any further comments? Be as imaginative as you can in answering this question. [5%]

(12) In typical injection molded parts, defects such as sink marks and weld lines may exist. What are the origins of these defects? How would these defects be avoided in terms of part/mold design? [10%]