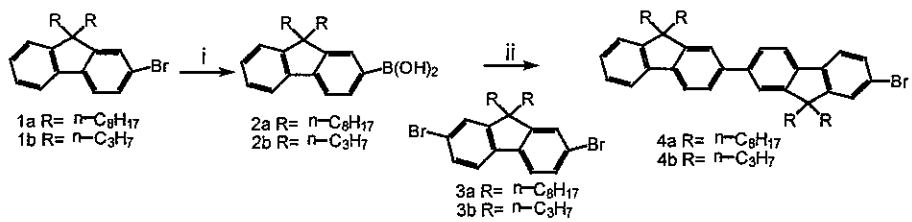
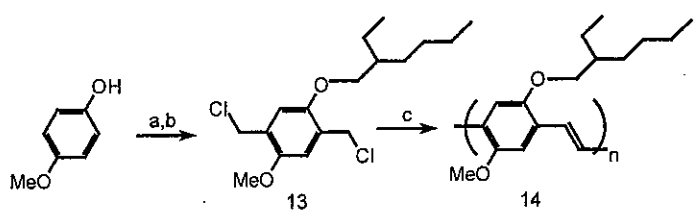
1. The first few steps of a recently proposed procedure [Katsis et al, *Chem. Mater.* **2002,** *14,* 1332] to obtain spiro-linked oligofluorenes as amorphous materials for blue light emission are given below.
   (1) These authors specifically noted that, in their experiments, tetrahydrofuran (THF) and toluene had been distilled over sodium/benzophenone and sodium, respectively. What are the roles of sodium and benzophenone, respectively, in the distillation procedure? **[10%]**
   (2) In practice, what is the usual method of maintaining a specific reaction temperature of –78 °C? **[5%]**
   (3) What is the purpose of brine washing? **[5%]**
   (4) In Step **ii**, what are the roles of $Pd(PPh_3)_4$, Na_2CO_3, toluene, and petroleum ether, respectively? **[20%]**



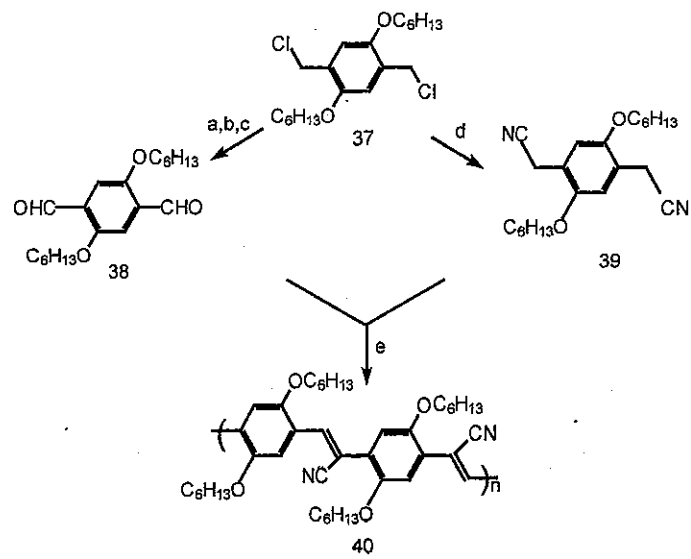
(i) To a solution of *2*-bromo-*9,9*-di-*n*-octylfluorene (**1a**, 12.0 g, 25.6 mmol) in anhydrous THF (50 mL) was slowly added *n*-BuLi (2.5 M in hexane, 12.0 mL, 30.0 mmol) at -78 °C. At this temperature, the reaction mixture was stirred for 1 h before adding tri-*iso*propyl borate (9.0 mL, 7.34 g, 39.0 mmol). It was then warmed to room temperature, stirred overnight followed by quenching with 100 mL HCl (2.0 M), and poured into a large amount of water. After extraction with ethyl ether three times, the organic portions were washed with brine before drying over anhydrous $MgSO_4$. Solid residues collected by evaporating off the solvent were purified by column chromatography on silica gel with petroleum ether/ethyl acetate (2:1) to afford 9,9-Di-*n*-octylfluorenyl-2-boronic acid (**2a**) as white solids (10.0 g, 89%).
(ii) A mixture of **2a** (2.0 g, 4.60 mmol), 2,7-dibromo-9,9-di-*n*-octylfluorene (**3a**, 4.0 g, 7.32 mmol), $Pd(PPh_3)_4$ (50 mg, 0.043 mmol), Na_2CO_3 (2.0 M aqueous solution, 12.0 mL, 24.0 mmol), and toluene (20 mL) was stirred at 90 °C for 2 days. After it was cooled to room temperature, 200 mL of petroleum ether was added to the reaction mixture. The organic portion was separated and washed with brine before drying over anhydrous $MgSO_4$. The solvent was evaporated off, and the solid residues were purified by column chromatography on silica gel with petroleum ether to afford 7-Bromo-9,9,9',9'-tetra- *n*-octyl-2,2'-bifluorene (**4a**) as white solids (2.52 g, 66%).

2. The Wudl procedure for the preparation of poly(*2*-methoxy-*5*-(*2'*-ethylhexyloxy)- *1,4*-phenylene vinylene) (MEH-PPV, see Structure **14**) from *4*-methoxyphenol is given below. The bis(chloromethyl) compound (**13**) is synthesized by alkylation of 4-methoxy-phenol (Step **a**) followed by chloromethylation (Step **b**). In Step **c**, polymerization of the monomer (**13**) is induced with a tenfold excess of potassium *t*-butoxide in tetrahydrofuran and gives the bright red-orange MEH-PPV (**14**). Careful control of concentration is needed to avoid gelation. Purification involves several reprecipitations in methanol.
   (1) Explain in a more detailed manner the reactions involved in Steps **a** and **b**, respectively, by writing down the mechanistic paths involved. **[20%]**
   (2) What is the mechanistic path of the reaction in Step **c**? **[10%]**



(**a**) *3*-(bromomethyl)heptane, KOH, EtOH, reflux, 16 h; (**b**) HCHO, concd. HCl, dioxane, 20 °C, 18 h, reflux, 4 h; (**c**) KO*t*Bu, THF, 20 °C, 24 h.

3. As shown below, the synthesis of CN-PPV (**40**), a cyano-modified poly(*2,5*-di- hexyloxy-*1,4*-phenylene vinylene), may be easily achieved via Knoevenagel condensation between equimolar amounts of the corresponding terephthaldehyde (**38**) and the benzene-1,4- diacetonitrile derivative (**39**), both obtained from the same starting material (**37**). The condensation reaction takes place at 50 °C upon addition of excess tetrabutylammonium hydroxide (or potassium *tert*-butoxide) in a mixture of tetrahydrofuran (THF) and *tert*-butanol. The product polymer (**40**) precipitates and can be easily isolated. Careful control of reaction conditions is required to avoid Michael additions (and consequently cross-linking). Purification is achieved typically by re-precipitation.
   (1) What is the mechanistic path of the reaction in Steps **a** to **c**? **[10%]**
   (2) What is the mechanistic path of the reaction in Step **d**? **[10%]**
   (3) Explain in detail the term 'Michael addition'. How would its occurrence lead to cross-linking in the present case? **[10%]**



(**a**) NaOAc; (**b**) KOH, EtOH; (**c**) pyridinium chlorochromate; (**d**) NaCN; (**e**) KOtBu or Bu_4NOH, tBuOH, THF, 50 °C.

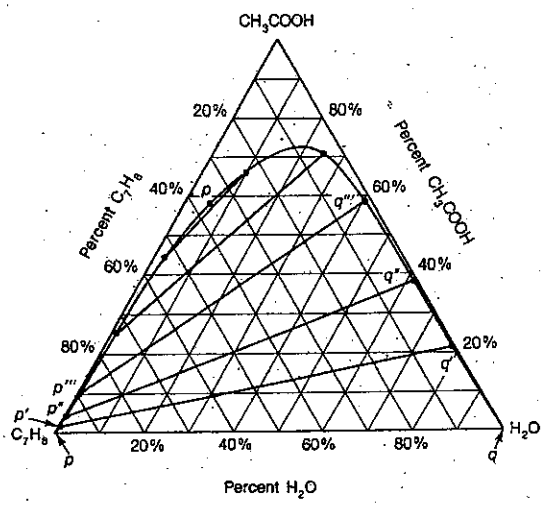
1. An ideal gas thermometer and a mercury thermometer are calibrated at 0°C and at 100°C. The thermal expansion coefficient for mercury is

$$\alpha = \left(\frac{1}{V_0}\right)\left(\frac{\partial V}{\partial T}\right)_p = 1.817\times10^{-4} + 5.90\times10^{-9}\theta + 3.45\times10^{-10}\theta^2$$

where θ is the Celsius temperature and $V_0 = V$ at θ = 0. What temperature would appear on the mercury scale when the ideal gas scale reads 50°C. (6%)

2. The vapor pressure of pure ethylene dibromide is 172 mmHg and that of pure propylene dibromide is 128 mmHg at 358 K and 1 atm. If these two components follow Raoult's law, estimate the total vapor pressure in kPa and composition of a solution that is 0.600 mol fraction propylene dibromide. (133.33 Pa/mmHg) (6%)

3. The isobaric solubility diagram for the system acetic acid-toluene-water is shown in the right Figure. What phase(s) and their composition(s) will be present if 0.2 mol of toluene is added to a system consisting of 0.5 mol of water and 0.3 mol of acetic acid? Give the relative amounts of each phase. (6%)



4. At 18°C the electrolytic conductivity of a saturated solution of CaF_2 is $3.86 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$, and that of pure water is $1.5 \times 10^{-6}\ \Omega^{-1}\ cm^{-1}$. The molar ionic conductivities of $1/2Ca^{2+}$ and F^- are 51.1 $\Omega^{-1}\ cm^2\ mol^{-1}$ and 47.0 $\Omega^{-1}\ cm^2\ mol^{-1}$, respectively. Calculate the solubility of CaF_2 in pure water at 18°C and the solubility product. (6%)

5. The following thermodynamic data apply to the complete oxidation of butane at 25°C:

$$C_4H_{10}(g) + 13/2O_2(g) \rightarrow 4CO_2(g) + 5H_2O(l) \qquad \Delta H^\circ = -2877\ kJ\ mol^{-1} \qquad \Delta S^\circ = -432.7\ J\ K^{-1}\ mol^{-1}$$

Suppose that a completely efficient fuel cell could be set up utilizing this reaction. Calculate (a) the maximum electrical work and (b) the maximum total work that could be obtained at 25°C. (6%)

6. Calculate the maximum wavelength of the radiation that will bring about dissociation of a diatomic molecule having a dissociation energy of 390.4 kJ mol^{-1}. (6%)

7. Calculate the wavelength and energy corresponding to the n = 4 to n = 5 transition in the hydrogen atom. (4%)

8. Calculate the percentage ionic character of the HCl, HI, and CO bonds from the following data: (6%)

	HCl	HI	CO
Internuclear distance/pm	127	160	113
Dipole moment/10^{-30} C m	3.60	1.40	0.33

9. Consider the following molecules H_2, CO_2, H_2O, CH_3Cl, H_2O_2, NH_3. Which of them will give a) a pure rotational spectrum, b) a vibrational-rotational spectrum, c) a pure rotational Raman spectrum, d) a vibrational Raman spectrum? (6%)

10. The speed that a body of any mass must have to escape from the earth is $1.07 \times 10^4\ m\ s^{-1}$. At what temperature would the average speed of (a) an H_2 molecule and (b) an O_2 molecule be equal to this escape speed? (6%)

11. (a) Determine the efficiency of area utilization in packing circles onto the lattice points of a square lattice. (b) Compare that value with the efficiency of packing circles onto a triangular lattice. (c) Which packing uses area more efficiently and by how much? (6%)

12. The composition of a protein corresponds to 5 mol of molar mass 30,000 g mol^{-1} and 10 mol of molar mass 60,000 g mol^{-1}. Calculate the number-average and mass-average molar masses. (6%)

(Physical constants: Avogadro constant $6.022 \times 10^{23}\ mol^{-1}$; Planck constant 6.626×10^{-34} J s; Rydberg constant $1.097 \times 10^7\ m^{-1}$; Boltzmann constant $1.381 \times 10^{-23}\ J\ K^{-1}$; Speed of light in vacuum $2.998 \times 10^8\ m\ s^{-1}$; Elementary charge 1.602×10^{-19} C)
(Atomic weight: Ca 40.08; F 19.00; H 1.008; O 16.00)

Multiple-Choice Questions (3% each)

13. Which of the following cannot affect the extent of reaction? (A) changing the temperature (B) adding a catalyst (C) increasing the amounts of reactants (D) removing some product (E) changing the volume.

14. In which of the following cases is the reaction expected to be exothermic? (A) Increasing the pressure increases the amount of product formed. (B) Increasing the amount of reactants increases the amount of product formed. (C) Increasing the temperature increases the amount of product formed. (D) Increasing the volume decreases the amount of product formed. (E) Increasing the temperature decreases the amount of product formed.

15. 6.00 moles of nitrogen gas and 6.00 moles of oxygen gas are placed in a 2.00-liter flask at 500°C and the mixture is allowed to reach equilibrium. What is the concentration, in moles per liter, of nitrogen monoxide at equilibrium if the equilibrium constant is found to be 4.00? (A) 3.00 M (B) 6.00 M (C) 8.00 M (D) 10.0 M (E) 12.0 M

16. A reaction in which the rate and the rate constant have the same units is (A) a radioactive decay (B) a second-order reaction (C) a reaction with a one-step mechanism (D) a first-order reaction (E) a zero-order reaction

17. Which of the following will be most helpful in determining the stability or shelf life of a new drug? (A) the reaction mechanism for its decomposition (B) the rate law for its decomposition (C) the Arrhenius plot of the decomposition reaction (D) the integrated rate law plot (E) the overall chemical reaction

18. A rate law is found to be $\text{Rate} = k[A]^2[B]$ Which of the following actions will not change the initial reaction rate? (A) doubling the concentrations of both A and B (B) doubling the concentration of A and halving the concentration of B (C) halving the concentration of A and doubling the concentration of B (D) halving the concentration of A and quadrupling the concentration of B (E) doubling the concentration of A and quadrupling the concentration of B

19. Which of the following changes will decrease the rate of collisions between gaseous molecule of type A and B in a closed container? (A) Decrease the volume of the container. (B) Increase the temperature of the system. (C) Add A molecules. (D) Take away B molecules. (E) Add a catalyst.

20. Of the following, which can be precisely determined for a chemical substance? (A) entropy, S (B) enthalpy, H (C) free energy, G (D) internal energy, E (E) all of these

21. The rate of reaction will be large if (A) $\Delta G°$ is a large negative number (B) $\Delta S°$ is a large negative number (C) $\Delta H°$ is a large negative number (D) K_{eq} is a large positive number (E) None of the above can be used to estimate reaction rates.

22. In expanding from 3.00 to 6.00 liters at a constant pressure of 2.00 atmospheres, a gas absorbs 100.0 calories. (24.14 calories = 1 liter·atm) The change in energy, ΔE, for the gas is (A) –600 calories (B) -100 calories (C) –44.8 calories (D) 44.8 calories (E) 100 calories

國立中山大學九十一學年度碩士班招生考試試題

科目：工程數學(甲)（材料所：乙組）

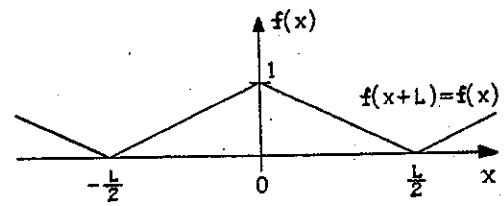
1. Try to solve the following equation. (20%)

$$y'' + 2y' + y = -3e^{-x} + 8xe^{-x} + 9.$$

2. Find the Eigenvalues and Eigenvectors. Also find a matrix Y that will diagonalize X, and determine the diagonalized X. (20%)

$$X = \begin{bmatrix} -1 & 4 \\ 0 & 3 \end{bmatrix}$$

3. Find the Fourier series for the plot shown below. (20%)

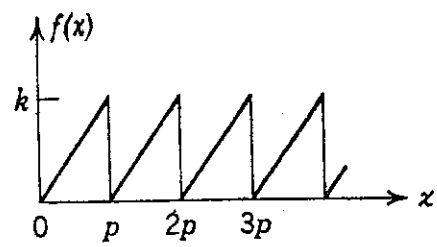


4. Solve the intergral equation. (20%)

$$f(x) = x^2 + \int_0^x \sin(x-u)\, f(u)\, du$$

5. Find the Laplace transformation of the function, (20%)

$$f(x) = \frac{k}{p}x \quad (\text{when } 0<x<p) \quad \text{and} \quad f(x+p) = f(x)$$



國立中山大學九十一學年度碩士班招生考試試題

科目：材料力學（材料所）（乙組）

Extrance examination, subject:Strength of materials

下列每題二十分

1. A cantilever beam with its length ℓ, carries a uniformly distributed load over the portion b measured from the root. Find the deflection of the free end and the spring constant of the beam.

2. You are given a circular cantilever beam with its length ℓ, along x-axis, vertical axis along y and radius r. When the beam experiences a moment in z direction, Mz, and a torque T in x direction please determine the slope, θ (in x and z directions) of the top surface of the free end

3. You are given a pure shear condition, where σ_{xz}, and σ_{yz} exist only. Please calculate the principal stresses and maximum shear stress.

4. A solid steel shaft with a fly wheel at one end rotates at constant speed n =120 rpm. If the bearing at the other free end suddenly freezes, what maximum shear stress and principal stresses will be produced in the shaft due to dynamic effects? Assuming shaft length ℓ = 5 ft, diameter, d = 2in., the weight of the flywheel W = 100lb, and its radius of gyration i = 10in.

5. please tell and demonstrate what are Young's modulus, Possion's ratio and bulk modulus.

國立中山大學九十一學年度碩士班招生考試試題

科目：工程數學（乙）（材料所）（丙組）

1. Try to solve the equation. (20%)

$$y'' - 2y' + y = e^x + x.$$

2. Find the inverse matrix A^{-1}. (20%)

$$A = \begin{bmatrix} 1 & 0 & 1 & 0 \\ 2 & -1 & 0 & 2 \\ -1 & 0 & 0 & 1 \\ 4 & 1 & -1 & 0 \end{bmatrix}$$

3. Find the Fourier series of the following function. (20%)

$$f(x) = |x|, \quad -\pi \le x \le \pi.$$

4. Solve the following integral equation. (20%)

$$f(x) = \sin 2x + \int_0^x f(u) \sin 2(x-u)\, du$$

5. Find the volume of the tetrahedron (not parallelepiped) with a, b, and c as adjacent edges with respect to right-handed Cartesian coordinates, (20%)

$$\mathbf{a} = \mathbf{i} + 2\mathbf{k}, \quad \mathbf{b} = 4\mathbf{i} + 6\mathbf{j} + 2\mathbf{k}, \quad \mathbf{c} = 3\mathbf{i} + 3\mathbf{j} - 6\mathbf{k}$$

國立中山大學九十一學年度碩士班招生考試試題

科目：熱力學（材料所碩士班）（丙組）

1. Derive the following equation from the change of entropy between any two states of an ideal gas with constant specific heat.
$$\Delta S = C_P \ln(V_2/V_1) + C_V \ln(P_2/P_1)$$ (15%)

2. (a) Calculate the work done *by* the system of mercury when the external pressure is changed from 0 to 10^8 N/m^2 at constant T. Calculate also (b) the heat flow out of the system as well as (c) the change in internal energy. For mercury at 273 K, the coefficient of expansion $\alpha = 1.81 \times 10^{-4}$ K^{-1}, the coefficient of compressibility $\beta = 3.88 \times 10^{-11}$ m^2/N, $C_P = 27.9$ J/ Kmol and $V = 1.47 \times 10^{-5}$ m^3/mol. Assume that these data are insensitive to pressure change. (20%)

3. Prove that as the temperature decreases to 0 K, the free energy change of a reaction (ΔG) approaches its enthalpy change (ΔH) at constant temperature. (5%)

4. (a) Derive the Clapeyron equation.
(b) When the pressure is increased, what will happen to the *melting* temperature of ice? What will happen to the *boiling* temperature of water? Explain. (30%)

5. A gas obeys the equation $P(V - b) = nRT$, where b is a positive constant.
(a) Show that $(\partial U/\partial V)_T = (\partial U/\partial P)_T = 0$.
(b) Show that $C_P = C_V + nR$.
(c) Show that for an adiabatic process $P(V - b)^\gamma$ = constant. (30%)

國立中山大學九十一學年度碩士班招生考試試題

科目：應用數學（材料所）（丁組）

1. Evaluate the following integral. (10%)

$$\int_{-\infty}^{\infty} \frac{dx}{(1+x^2)^3}$$

2. Evaluate the following integral. (10%)

$$\int_{-\infty}^{\infty} \frac{e^{i\omega t}}{\omega^2 - \omega_o^2} d\omega, \quad \text{with } t > 0$$

3. Try to solve the following equation. (20%)

$$y'' + y = \sec x.$$

4. Find the Eigenvalues and Eigenvectors. Also find a matrix N that will diagonalize M, and determine the diagonalized M. (20%)

$$M = \begin{bmatrix} -1 & 4 \\ 0 & 3 \end{bmatrix}$$

5. Find the Fourier integral. (20%)

$f(x) = e^{-kx}$ when $x>0$, and $f(-x) = f(x)$
and when $x>0$, and $f(-x) = -f(x)$

6. Solve the following equation, and express f(x) in terms of g(t), where g(t) is an intergrable function. (20%)

$$f(x) + \int_0^{\infty} f(t) \sin(x-t)\, dt = g(x)$$

1. An ideal gas at 300 K occupies a volume of 0.5 m^3 at a pressure of 2 atm. The gas expands adiabatically until its volume is 1.2 m^3. Next the gas is compressed isobarically up to its original volume. Finally the pressure is increased isochorically until the gas returns to its initial state. (a) Determine the temperature at the end of each transformation. (b) Find the work done during the cycle. [14%]

2. Two walls of thicknesses of L_1 and L_2 and thermal conductivities K_1 and K_2 are in contact. The temperatures at the outer surfaces are T_1 and T_2. Compute the temperature at the common wall. Assume steady conditions. [10%]

3. What is the main difference between (a) metals and semimetals, and (b) semiconductors and insulators? Also, explain the temperature dependence of resistivity for the metal and semiconductor. [18%]

4. Give a precise definition of the time constant of a circuit. Express the time constant of an RL- and an RC-circuit. Does an RCL-circuit have a time constant? [13%]

5. Justify, in terms of energy considerations, why in the Compton effect the scattered radiation has a longer wavelength than the incident radiation. [7%]

6. Discuss the possible processes that may occur when (a) an atom, (b) a molecular, and (c) a nucleus interacts with a photon. Discuss the possible interactions as a function of photon energy. [18%]

7. A charged conductor contains an empty cavity. Show that the electric field inside the cavity is zero and that the charge on the inner surface is also zero. [10%]

8. The arrangement of a mass spectrometer is shown in the figure below. The ions, after crossing the slits, pass through a velocity selector composed of an electric field **E** produced by the charged plates P_1 and P_2, and a magnetic field **B** perpendicular to the electric field. Those ions pass undeviated through the crossed fields enter into a region where a second magnetic field **B'** exists, and bent into circular orbits. A photographic plate registers their arrival. Show that q/m = **E**/r**BB'**. [10%]