1) For the substitution reaction between t-butyl chloride and sodium hydroxide the following experimental observations have been made:
   a) The rate is dependent only on the concentration of the t-butyl chloride.
   b) There is an increase in the reaction rate when the methyl hydrogens of t-butyl chloride are replaced by alkyl groups.
   c) When methyl hydrogens are replaced by flourines, a substantial reduction in rate is observed.

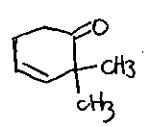
   What do these observations suggest about the transition state of this reaction ? (15 %)

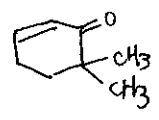
2) Optically pure alkyl halides cannot be made easily from optically pure tosylates and halide ion. An S_N2 exchange process between product and halide ion results in racemization. Racemization is a more serious problem for the preparation of an alkyl bromide and iodide than for an alkyl chloride. Suggest an explanation. (15 %)

3) Draw the structure of each of the following compounds and indicate whether it is a primary, secondary, or tertiary alcohol, ether, or alkyl halide:
   a) 2-methyl-2-butanol, b) 3–methoxyhexane, c) 2-chloro-2-methylpentane d) methyl neopentyl ether, e) 4-ethyl-3-hexanol. (20 %)

4) How would you use IR to distinguish between each of the following pairs of isomers? For each member of the pair, quote one IR band position which should be present (or absent) and which can be used to distinguish the substance from its isomer.

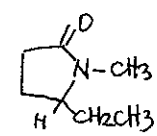
a)

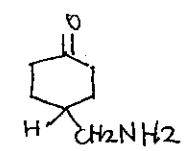




(5 %)

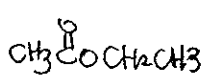
b)

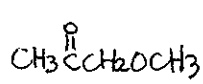




(5%)

c)



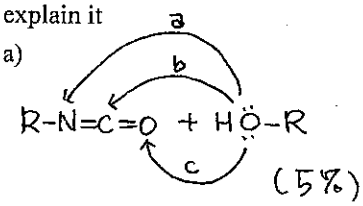


(5 %)

(continued)

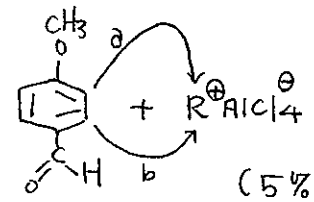
5) In the following reactions, there are different possible reaction pathways (a, b or c). Please indicate which of the pathway is the most probable one in each set and explain it

a)



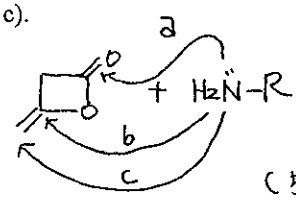
(5%)

b)



(5%)

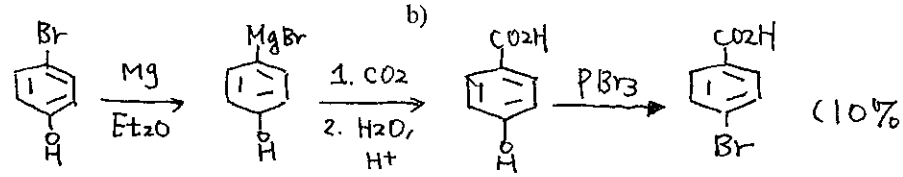
c).



(5%)

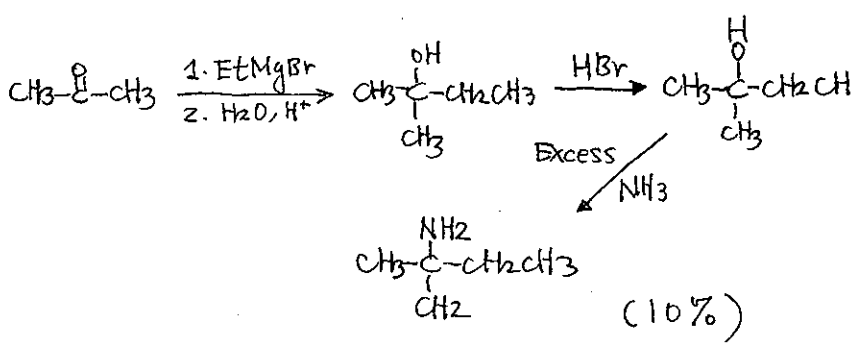
6) In each of the following syntheses, there is at least one incorrect step. Identify the incorrect steps and explain what is wrong with each.

a) b)



(10%)

b)



(10%)

國立中山大學八十八學年度碩博士班招生考試試題

科　目：工程數學（材料科學研究所碩士班）　　共 1 頁 第 1 頁

Please note that (1) *a calculator can be used for this test*, (2) *partial credits will be given* ***only*** *to incomplete answer relevant to the solution of the problem*, and (3) *each problem is worth 20 points.*

1. (***Linear Algebra***) In a cartesian coordinate system, any position in space can be identified using mutually orthogonal unit vectors $\hat{x}$, $\hat{y}$ and $\hat{z}$. If this coordinate system undergoes a rotational transformation to $\hat{x}'$, $\hat{y}'$ and $\hat{z}'$ with

$$\hat{x}' = \frac{1}{\sqrt{3}}\hat{x} + \frac{1}{\sqrt{3}}\hat{y} - \frac{1}{\sqrt{3}}\hat{z},$$

$$\hat{y}' = \frac{1}{\sqrt{2}}\hat{x} + \frac{1}{\sqrt{2}}\hat{z},$$

please find $\hat{z}'$.

2. (***Integration***) Please evaluate $\iiint_v F(x,y,z)\,dx\,dy\,dz$, where $F(x,y,z) = e^{-(x^2+y^2+z^2)^3}$

and v the volume bounded by the two spheres $x^2+y^2+z^2=1$ and $x^2+y^2+z^2=3$.

3. (***Fourier Series***) A simple full-wave rectifier can be considered as having passed the positive peaks of an incoming *sine* wave and inverting the negative *sine* peaks. This yields

$$f(t) = \begin{cases} \sin\omega t, & 0 < \omega t < \pi, \\ -\sin\omega t, & -\pi < \omega t < 0. \end{cases}$$

Please find the Fourier series of this rectifier function $f(t)$.

4. (***Differential Equation***) A simple series *RLC* circuit obeys the following time derivative differential equation of the current *I*.

$$L\ddot{I} + R\dot{I} + C^{-1}I = 0$$

Assume a current solution in the form of $I = I_o e^{\alpha t}$, please find the conditions of *RLC* for the current *I* being (1) steady oscillation and (2) damped oscillation.

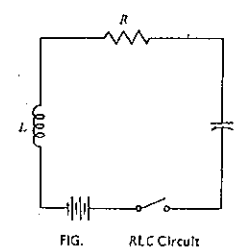


FIG. RLC Circuit

5. (***Statistics***) Consider a random experiment, the outcome can be classified in either *success* or *failure*. If this random experiment is repeated a number of times so that (1) the outcomes of these trials are mutually independent, and (2) the probability of success p is the same for each trial. Then, for n trials with y successes occur, the probability distribution function is called *binomial distribution* $b(n, y)$.

$$b(n,y) = \frac{n!}{y!\,(n-y)!} p^y (1-p)^{(n-y)}$$

As the number of trial becomes large ($n \to \infty$), and the probability of *success* becomes small ($p \to 0$), please prove the Poisson distribution function given as

$$\lim_{\substack{n\to\infty \\ p\to 0}} b(n,y) = \frac{(np)^y e^{-np}}{y!}$$

1. (a) A system consists of three energy levels—a ground level ($E_0 = 0$, $g_0 = 1$), a first excited level ($E_1 = 2kT$, $g_1 = 3$), and a second excited level ($E_2 = 6kT$, $g_2 = 2$). Determine the partition function. (b) What is the probability for the second level? (c) What is the ratio of the number of particles in each of the levels? (d) Assume that the system described in part (a) contains 1 mole of particles. How many particles are in each level? (20%)

2. (a) A 25.00 ml aliquot of 1.00 M NaOH and a 10.00 ml aliquot of 0.50 M NaCl were mixed. What are the concentrations of the compounds in the resulting solution? Assume that the volume of the resulting solution is 35.00 ml. (b) What are the concentrations of the ions in the resulting solution? (10%)

3. When alkanes are heated up, they lose hydrogen and alkenes are produced. For example,

   $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$ K = 0.36 at 1000 K

   If this is the only reaction that occurs when ethane is heated to 1000 K, at what total pressure will ethane be (a) 10% dissociated and (b) 90% dissociated to ethylene and hydrogen? (10%)

4. Given the following fundamental frequencies of vibration, calculate ΔH° for the reaction

   $H^{35}Cl\ (v=0) + {}^2D_2\ (v=0) \rightleftharpoons {}^2D^{35}Cl\ (v=0) + H^2D\ (v=0)$

   $H^{35}Cl$: 2989 cm^{-1} H^2D : 3817 cm^{-1}

   ${}^2D^{35}Cl$: 2144 cm^{-1} ${}^2D^2D$: 3119 cm^{-1} (10%)

5. A gas reaction 2A = B is second order in A and goes to completion in a reaction vessel of constant volume and temperature with a half life of 1 hour. If the initial pressure of A is 1 bar, what are the partial pressures of A, of B, and the total pressure at 1 hour, 2 hours, and at equilibrium? (10%)

6. One mole of an ideal gas ($\overline{C}_p = 5R/2$) is expanded adiabatically from 600 K at 7.00 atm to a final pressure of 1.00 atm. Find ΔE and ΔH for this change if the expansion is

   (a) Reversible

   (b) Irreversible against a constant pressure of 1 atm. (15%)

7. How do glues and adhesives work? (10%)

8. Find ΔH_{1000} for $2H_2(g) + O_2(g) \longrightarrow 2H_2O(g)$ from the following data; $\bar{C}_p = a + bT + cT^{-2}$ (J mol^{-1}) and $\Delta H^\circ_{298} = \Delta H^\circ_f = -241.83$ J mol^{-1}. (15%)

Item	$2H_2$	O_2	$2H_2O$	Δ (Item)
ΔH°_f	0	0	2(-241.83)	-483,660
a	2(27.3)	30.0	2(30.5)	-23.6
b x 10^3	2(3.3)	4.2	2(10.3)	9.8
c x 10^{-5}	2(0.50)	-1.7	0	0.67

Gas constant, R = 8.314 J K^{-1} mol^{-1}

Planck's constant, h = 6.6256 x 10^{-34} J s

25% for each problem.

1. If the stress state at a point is σ_{xx} = 1000 psi, τ_{xz} = 500 psi, σ_{yy} = 0 , τ_{xy} = 0, σ_{zz} = 500 psi, τ_{yz} = 0 , what are the principal stresses at the point and their corresponding directions?
2. In Fig.P2 is shown a composite bar having a diameter of 2 in. Material *a* is to be considered a linear, elastic material with a Young's modulus of 20×10^6 psi and a linear thermal coefficient of expansion 6×10^{-6} /°F. Material *b*, however, is to be considered to behave in an elastic, perfectly plastic manner (neglecting the strain-hardening effect) with E= 30×10^6 psi, a yield stress of 50,000 psi, and a linear thermal coefficient of expansion equal to 12×10^{-6} /°F. If the temperature is changed from 60° to 100°F, what is the thermal stress? What is the maximum stress possible for this system?
3. A 45000 N force (Fig.P3) acts on a rod *A* having a modulus of elasticity E of 7×10^{10} Pa. The diameter of *A* is 50 mm and the length is .3 m. A sleeve *B* restrains *A* through a rigid plate *C*. The mean radius of *B* is .1 m and its thickness is 2.5 mm. The length of *B* is .2 m. If *B* has a modulus of elasticity in compression of 1.4×10^{11} Pa, what is the movement of the plate *C* and that of the end *D* ?
4. A torque of 3300 N-m is transmitted through a 50-mm-diameter solid shaft having a yield stress in shear of 1.1×10^8 Pa. Is there plastic deformation for this loading? If so, how far has the plastic action penetrated from the surface assuming elastic, perfectly plastic behavior? What is the maximum possible static moment?

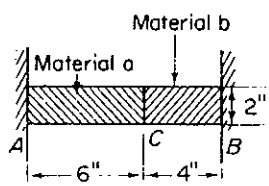


Figure P2

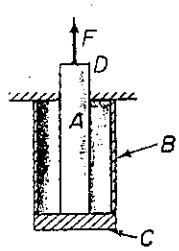


Figure P3

國立中山大學八十八學年度碩博士班招生考試試題

科　目：熱力學　材料所 丙組

請於答案券上依序作答，並清楚標明題號

1. The system move from one state to another one and obtain the work as PΔV. Which is the process path, (a) constant-volume process, (b) constant-pressure process, (c) constant-temperature process, and (d) adiabatic process. (5%)
2. Determine which of the following properties of a thermodynamic system are extensive properties and which are intensive. (a) the mass density, (b) the molar density, (c) the number of gram atoms of aluminum in a chunk of alumina, (d) the potential energy of a system in a gravitational field, (e) the molar concentration of NaCl in a salt solution, and (f) the heat absorbed by the gas in a cylinder when it is compressed. (20%)
3. An ideal gas changes from state (P_1,V_1) to state (P_2,V_2) isothermally. What is the change of the internal energy? (5%)
4. The van der Waals equation for one mole of gas, $(P + a/V^2)*(V-b)=RT$. Briefly describe the meaning of the correction term a/V^2 and b. (15%)
5. A Carnot engine operates between 180 °C and 60 °C performs 1000 joules of work. Calculate the efficiency of the engine and the heat input to the engine.(15%)
6. A 50 kg steel casting at a temperature 500 °C is quenched in 200 kg of oil initially at 20 °C. Assuming no heat losses and the steel casting and oil to have constant specific heats of 0.5 and 2.5 kJ/kg-°K respectively. Calculate the oil equilibrium temperature. (20%)
7. The total differential of the function $G = 4\,T^3*y*\cos(x)$ and $dG = AdT + Bdy + Cdx$. What is the value of C and A. (20%)