國立雲林科技大學 108 學年度 系所：化材系
碩士班招生考試試題 科目：物理化學

1. For the reversible process of the gas [C_V (heat capacity of constant volume) = constant] which is in a closed system and obeys the following equation of state:

$$P(V-b) = nRT \qquad \text{where } b \text{ is a constant}$$

according to the first law of thermodynamics and Maxwell relation (obtained from $dA = -SdT - pdV$), show that $\Delta U = C_V \Delta T$, where ΔU is the changes of internal energy for the gas and ΔT is the changes of temperature for the gas. (24 %)

2. For a regular solution in which the mole fraction of A is x_A and the mole fraction of B is x_B, show that the Gibbs energy of mixing (its temperature is T, n is total moles, and β is a parameter) is $\Delta_{\text{mix}}G = nRT(x_A \ln x_A + x_B \ln x_B + \beta x_A x_B)$. (12%)

3. The following consecutive reactions are elementary:

$$\mathrm{A} \xrightarrow{k_a} \mathrm{I} \xrightarrow{k_b} \mathrm{P}$$

If the initial concentration of A is $[A]_0$ and no I as well as P are present initially. When $\mathrm{A} \rightarrow \mathrm{I}$ is the rate-determining step ($k_a \ll k_b$). Find an approximate expression for the concentration of P as a function of the time. (14%)

4. Two mole of a perfect gas at 300 K is allowed to expand reversibly and isothermally from 10 dm^3 to 100 dm^3. (a) What is the change of entropy of the gas and its surroundings? (b) The same gas is expanded adiabatically and irreversibly from 10 dm^3 to 100 dm^3 with no work done. What is the final temperature of the gas? What is the change of entropy of the gas and its surroundings? (12%)

5. The partial molar volumes of water and ethanol in a solution with at 303K are 16.2 and $58.8\,\text{cm}^3\,\text{mol}^{-1}$, respectively. The mole fraction of ethanol is 0.42. Calculate the volume change upon mixing sufficient ethanol with 2.65 mol of water to give this concentration. The densities of water and ethanol are 0.992 and $0.7823\,\text{g}\,\text{cm}^{-3}$, respectively, at this temperature. (12%)

6. The value of the equilibrium constant for the reaction $A(g) + B(g) \rightleftharpoons C(g)$ is 10.36 at 400K and 7.24 at 500K. Determine (a) the standard reaction enthalpy, (b) equilibrium constant, (c) standard reaction Gibbs energy and (d) standard reaction entropy for this reaction at 450K. (14%)

7. The rate equation for the chemical reaction: $A \rightarrow B + C$ is first-order with $k_r = 9.82\times10^{-6}\,\text{s}^{-1}$ at 300K and $2.84\times10^{-4}\,\text{s}^{-1}$ at 328K. Determine (a) the energy of activation and (b) the pre-exponential factor (frequency factor) for the reaction. (12%)

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系所：化材系
科目：單元操作與輸送現象

1. Please explain the following terms:
   (a) incompressible fluid (3%)
   (b) hydraulic radius (3%)
   (c) kinematic viscosity (3%)
   (d) Newtonian fluid (3%)
   (e) friction factor (3%)

2. A packed bed is composed of cylinders having a radius R = 0.01 m and a length h = 0.02 m. The bulk density of the overall packed bed is 950 kg/m^3 and the density of the solid cylinders is 1600 kg/m^3.
   (a) What is the void fraction? (3%)
   (b) What is the effective diameter of the particles? (6%)
   (c) What is the ratio of total surface area in the bed to total volume of bed (void volume plus particle volume)? (6%)

3. In a process in which A is used as a solvent, it is evaporated into dry nitrogen. At 300 K and 101.3 kPa, the resulting mixture has a percentage relative humidity of 50. It is required to recover 85 % of the A present by cooling to 285 K and compressing to a suitable pressure. What should this pressure be?（20%）

   Vapor pressure of A at 300 K = 12.3 kPa; at 285 K = 6 kPa

   Molecular weight of A = 80 g/mole

4. A copper sphere of radius R and thermal conductivity k is initially in equilibrium at 500 K in a hot oil bath. It is suddenly removed from the bath and cooling in air at 300 K. The convection heat transfer coefficient for this cooling process is h.
   (a) Write the conservation equation of the transient conduction occurs in the sphere. (6%)
   (b) What are the initial condition and the boundary conditions of this system? (3%)
   (c) Under what physical condition the temperature in the sphere can be regarded as uniform? (5%)
   (d) Write the approximate energy balance equation for the transient conduction in this solid sphere if the lumped capacitance method can be applied. (6%)

5. Gas A diffuses through a stagnant film of gas surrounding a catalyst particle. A undergoes the following reaction $2A \rightarrow B$ at the particle surface, instantaneously, B diffuses back through the stagnant film into the bulk. The catalytic surface is considered as a flat surface. Assuming isothermal conditions,
(a) obtain an expression for the local reaction rate in terms of the effective gas-film thickness (δ) and the bulk gas stream compositions X_{Ao} and X_{Bo} (7%)
(b) evaluate the concentration profiles of A in the stagnant film. (8%)

6. Please give the SI units of the following terms:
(a) thermal conductivity (3%)
(b) heat transfer coefficient (3%)
(c) thermal diffusivity (3%)
(d) mass transfer coefficient (3%)
(e) Nusselt number (3%)

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科目：化工動力學

1. The reaction (A→B) is carried out in a CSTR, wherein the reaction data is listed as following. The species A enters the reactor at a molar flow rate of 0.5 mol/s. The entering volumetric flow rate is 0.002 m^3/s.

Conversion of A (%)	Reaction rate (mol/m^3-s)
0	0.45
10	0.37
20	0.30
40	0.195
60	0.113
70	0.079
80	0.040

(a) Please calculate the volume of CSTR to achieve 80% conversion of A. (13%)
(b) Please calculate the space time in hour to achieve 80% conversion of A. (6%)
(c) Please calculate the space velocity to achieve 80% conversion of A. (6%)

2. The reaction (A→C) is carried out in a CSTR, wherein the reaction data is listed as following. The species A enters the reactor at a concentration of 1.0 mol/L.

Reaction time (min)	Concentration of A in the reactor (mol/L)
0	1.000
0.5	0.855
1.0	0.730
1.5	0.624
2.0	0.533
3.0	0.390
4.0	0.285
6.0	0.152
10.0	0.043

(a) If the rate equation obeys first order ($-\gamma_A = kC_A$), please derive reaction time (t) as a function of conversion of A (χ) and evaluate the rate constant. (17%)
(b) If the rate equation obeys second order ($-\gamma_A = kC_A^2$), please derive reaction time (t) as a function of conversion of A (χ). (8%)

3. (25%) The gaseous reaction A → B is carried out in a tubular reactor system consisting of 10 parallel 10m long tubes with a 20cm inside diameter. Preliminary experiments have determined the reaction rate constant for this first-order reaction as 0.001 s^{-1} at 300K and 0.003 s^{-1} at 350K. A has a molecular weight of 100. Assuming ideal gas behavior is followed and no reverse reaction is happened. At what temperature the reaction rate constant can reached 0.01 s^{-1} and what conversion of A can be reached at this temperature with a feed rate of 3.14 ton/h of pure A and an operating pressure of 8.2 atm?

4. (15%) It is known that

$$A \longrightarrow B \qquad r_B = k_B C_A^2$$

$$A + B \longrightarrow 2C \qquad r_C = k_C C_A C_B$$

If C is the desired product, what is the instantaneous selectivity of C to B? What kind of reactor or reactor combinations and at what temperatures would you use for the reaction system?

$$C_{A0} = 4\ \text{mol/dm}^3\ \ k_B = 1\ \text{dm}^3/\text{mol}\cdot\text{min at 300K with } E = 4000\text{cal/mol}$$

$$k_C = 1\ \text{dm}^3/\text{mol}\cdot\text{min at 300K with } E = 12000\text{cal/mol}$$

5. (10%) Please briefly describe the characteristics, usage, advantages, and disadvantages of Plug Flow reactors (PFR) and Batch reactor.

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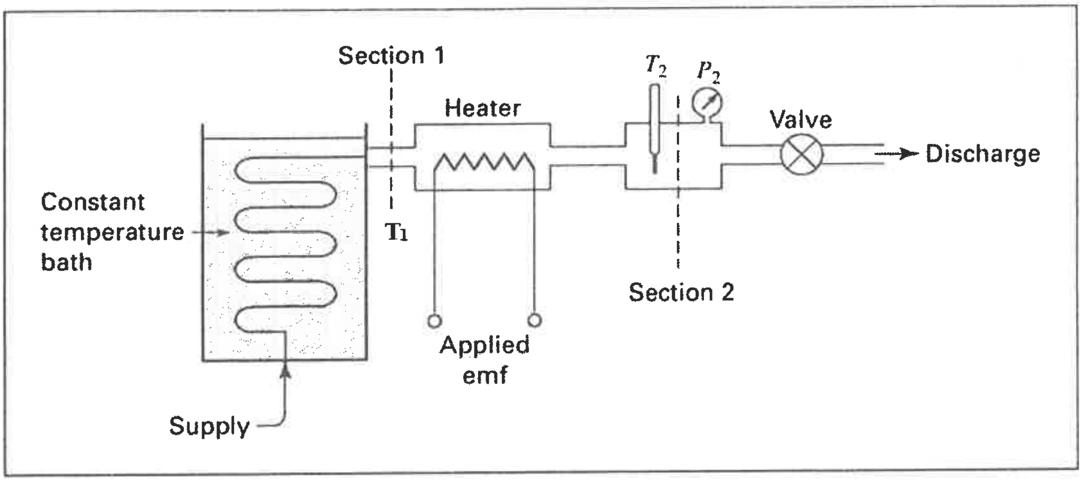
1. [9%]

A simple flow calorimeter is illustrated schematically in the figure below.



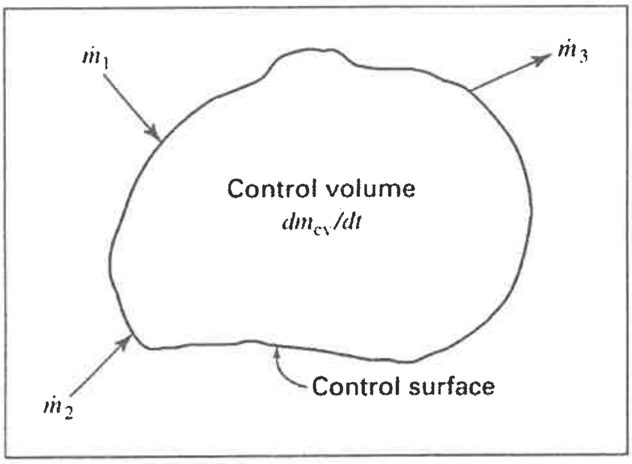
(1) What is the function for the flow calorimeter? [3%]

(2) Write the energy balance equation for the process, assuming that both kinetic- and potential energy are negligible and there is no shaft work. [3%]

(3) If the test fluid is water, flow rate = 4.15 g s^{-1}, T_1 = 0 ℃, T_2 = 300 ℃, P_2 = 3 bar, rate of heat addition from resistance heater = 12,740 W. The water is completely vaporized in the process. Calculate the enthalpy of steam at 300 ℃，3 bar based on H = 0 for $H_2O(l)$ at 0 ℃. [3%]

2. [18%]

According to the schematic representation of a control volume for an open system,



(1) What is the *continuity equation* for the mass balance? The expression should include $\frac{dm_{cv}}{dt}$ and u(velocity), A(cross-sectional area), ρ(density). [3%]

(2) What is the mathematical condition for a steady-state based on the equation given in (1)? [3%]

(3) Write the complete energy balance with a mathematical expression, including $\frac{d(mU)_{cv}}{dt}$, $\dot{m}$, enthalpy change(ΔH), $\dot{Q}$, and $\dot{W}$ (Assume potential energy and kinetic energy are negligible). [3%]

(4) What is the mathematical condition for a steady-state, steady-flow process based on the equation given in (3)? [3%]

(5) Write an energy balance equation for a steady-state, steady-flow process based on (3) if kinetic- and potential energy are negligible and the mechanical work is W_s only. [3%]

(6) Derive the expression for a closed system starting from (5). [3%]

3. 【9%】

Air flows at a steady rate through a horizontal pipe to a partly closed valve. The pipe leaving the valve is enough larger than the entrance pipe that the kinetic-energy change of the air as it flows through the valve is negligible. The valve and connecting pipes are well insulated. The conditions of the air upstream from the valve are 20℃(293.15 K) and 6 bar, and the downstream pressure is 3 bar. If air is regarded as an ideal gas, and the system is insulated, making Q negligible. The potential –energy and kinetic-energy changes are negligible.

(1) What is ΔH value for this process? [3%]

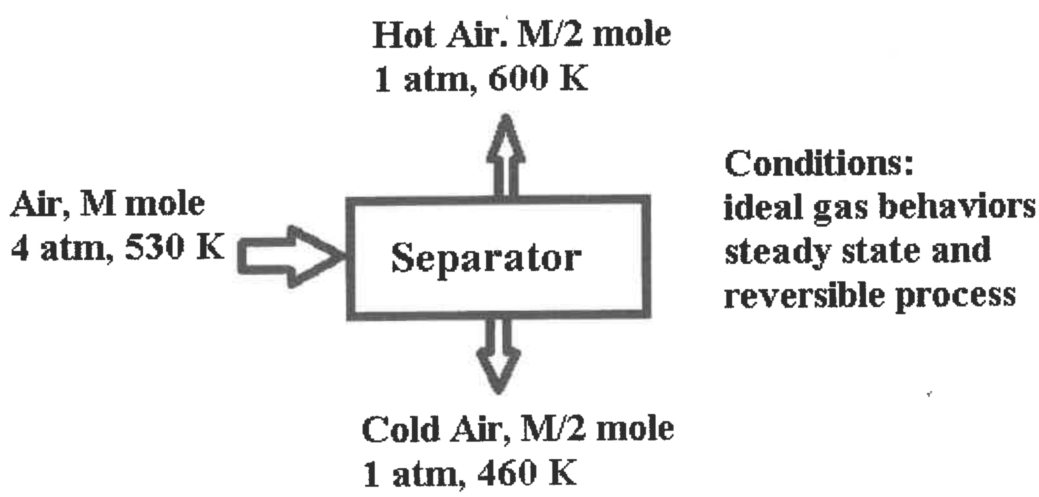
(2) What is the temperature of the air some distance downstream from the valve?

[3%]

(3) What is such a process called in chemical industrial application? [3%]

4. [9%]

The following illustrates one mole (M=1 mole) of gas separation process through a separating device and the conditions for the whole process. Assume Cp=(7/2)R, adiabatic and no shaft work. Please answer the following question.



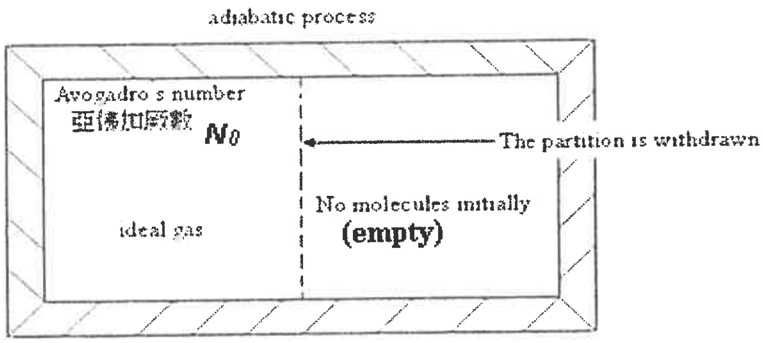
(1) What is the value of ΔS_1 for the process to the hot air? [3%]

(2) What is the value of ΔS_2 for the process to the cold air? [3%]

(3) Calculate ΔS_{total} for the whole process. Whether the whole process is possible? [3%]

5. [5%]

Suppose an insulated container, partitioned into two equal volumes, contains Avogadro's number N_0 of ideal-gas molecules in one section and no molecules in the other. When the partition is withdrawn, the molecules quickly distribute themselves uniformly throughout the total volume. The process is an adiabatic expression that accomplishes no work.



(1) What is the ΔT for this process? [2%]

(2) What is the ΔS for this process? [3%]

6. [25%]

For the binary system 1 and 2, the following Antoine equations provide vapor pressures:

$\ln P_1^{sat} = 14.28 - \dfrac{2943.3}{T/^{o}C + 223}$; $\ln P_2^{sat} = 14.21 - \dfrac{2975.5}{T/^{o}C + 210}$; where T is in kelvins and the vapor pressures are in kPa. Assume the validity of Rault's law,

(1) Prepare a graph showing p (pressure) vs. x_1 and p vs y_2 for a temperature of 76°C. [10%]

(2) Prepare a graph showing T (temperature) vs x_1 and T vs y_2 for a pressure of 72 kPa. [10%]

(3) Please address the bubble line, dew line, and phases in the graphs (1) and (2). [5%]

7. [10%]

For thermodynamic property M, we can know nM = M(T, P, $n_1, n_2, ..n_i...$), and $\overline{Mi}$ a generic partial property. Please show us how to obtain M= $\sum x_i \overline{M_i}$ and $\sum x_i d\overline{M_i} = 0$ at constant T and P.

8. [15%]

(1) Please explain what physical meanings of fugacity, fugacity coefficient, activity, and activity coefficient are, respectively? [8%]

(2) Please show how to gain the activity coefficient is a function of Poynting factor as a vapor mixture and a solution coexist in equilibrium. [7%]

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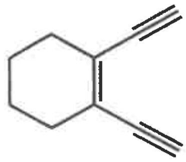
科目：有機化學

1. Consider the equilibrium

$$PO_4^{3-} + H_2O \rightleftharpoons HPO_4^{2-} + HO^-$$

Which are the Brönsted-Lowry bases? (6%, more than one answer, give scores depending on the degree of correctness)

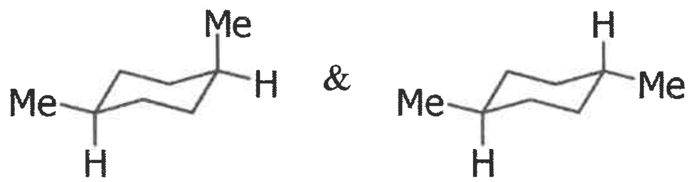
2. (a) Calculate the index of hydrogen deficiency (or degree of unsaturation) of the following molecule. (5%)



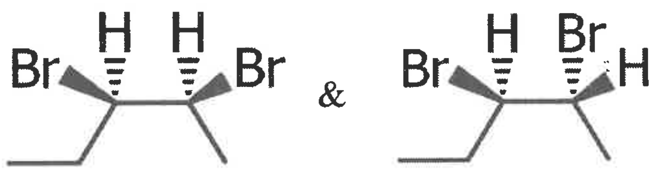
(b) Calculate the index of hydrogen deficiency (or degree of unsaturation) of a compound with the molecular formula of C_7H_7NOS. (5%)

3. Label the following pairs of molecules as enantiomers, diastereomers, or same molecule. (9%)

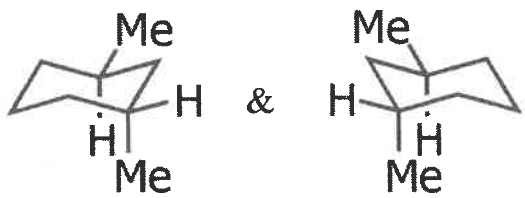
(a)



(b)



(c)



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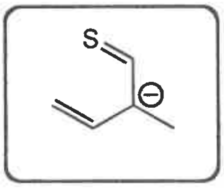
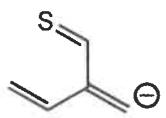
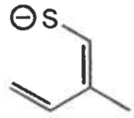
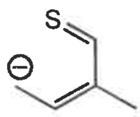
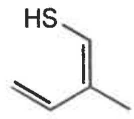
4. **Which of the following species are *not* a resonance form(s) of the anionic species in the box? (6%, more than one answer, give scores depending on the degree of correctness)**




I


II


III

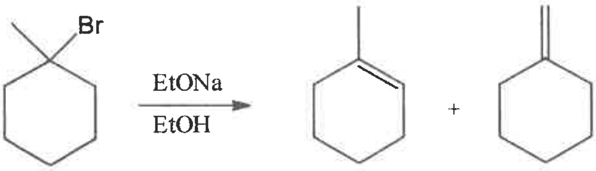

IV

5. **Which will be the major products of the following reactions? (9%)**

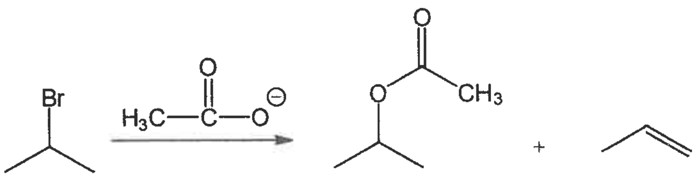
(a)

$$CH_3CH_2CHCH_3 \text{ (Br on C-2)} \xrightarrow[t\text{-BuOH}]{t\text{-BuOK}} CH_3CH{=}CHCH_3 + CH_3CH_2CH{=}CH_2$$

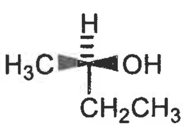
(b)

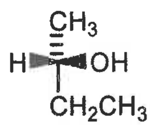


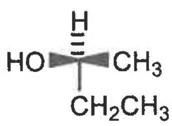
(c)

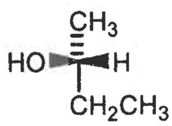


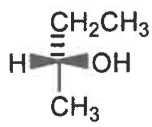
6. **Which of the following represent (*R*)-2-butanol? (10%, more than one answer, give scores depending on the degree of correctness)**


I


II


III


IV


V

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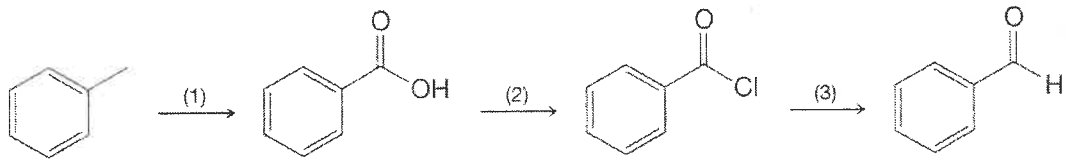
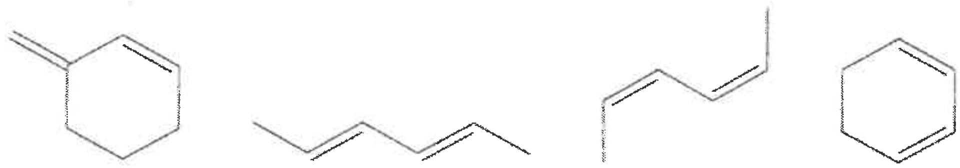
7. **Provide the reagents for transformations (1), (2), and (3). (15%)**

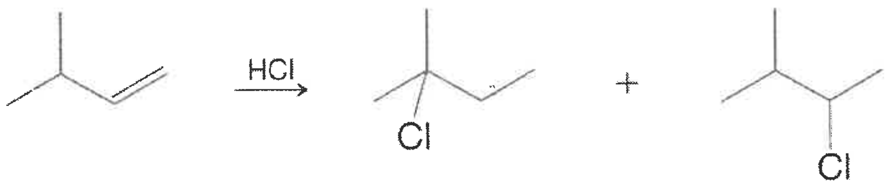


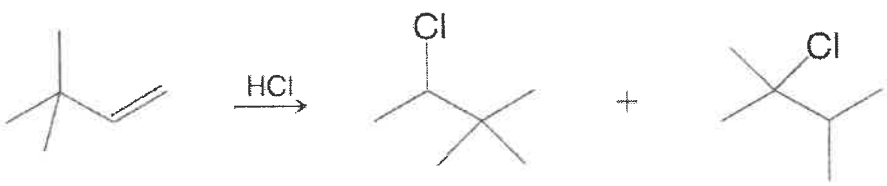
8. **When benzene reacts with 1-chloro-2,2-dimethylpropane (neopentyl chloride) in the presence of aluminum chloride, the major product is 2-methyl-2-phenylbutane, not 2,2-dimethyl-1-phenylpropane (neopentylbenzene). Explain this result. (10%)**

9. **Rank the following dienes in order of increasing reactivity in a Diels-Alder reaction (1 = least reactive, 4 = most reactive). Briefly explain your ranking. (5%)**



10. **Provide mechanistic explanations for the following observations: (10%)**

(a)


(b)


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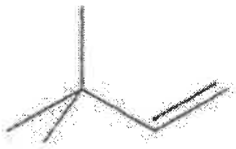
11. Starting with an appropriate alkyl halide and base, outline syntheses that would yield each of the following alkenes as the major (or only) product: (10%)

(a)



(b)