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國內初選筆試－選擇題答案卷

一、單選題：（每題 3 分，共 72 分）

題號	1	2	3	4	5	6	7	8
答案	B	D	D	A	C	B	C	B
題號	9	10	11	12	13	14	15	16
答案	C	E	D	D	送分	E	A	B
題號	17	18	19	20	21	22	23	24
答案	D	A	E	C	A	C	送分	B

二、多選題：（每題 4 分，共 68 分）

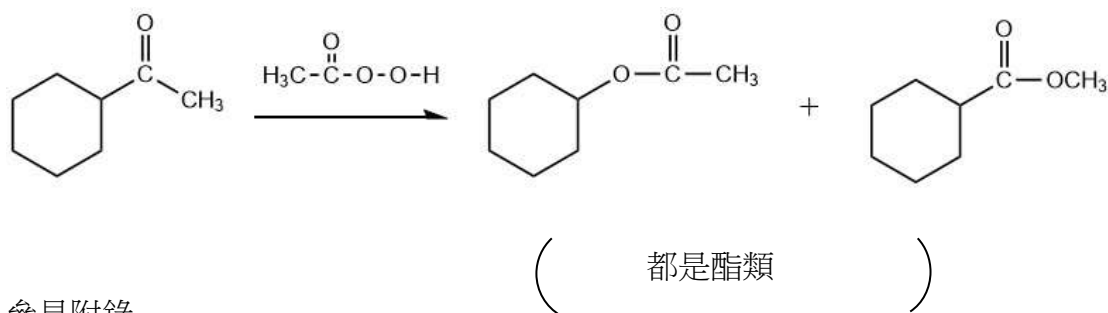| 題號	25	26	27	28	29	30	31	32
答案	AE	BDE	AC	CD	BCD	AB	ABCD	ACE
題號	33	34	35	36	37	38	39	40
答案	CDE	ABD	ABDE	ACDE	BE	ACE	ACDE	BD
題號	41							
答案	AC							

11. D 說明：答案誤值
13. 送分
23. 送分

26. BDE 說明：答案誤值

27.
甲苯與氯氣在 $FeCl_3$ 催化下，會形成兩種主要產物－鄰氯甲苯及對氯甲苯，因此(D)選項錯誤。

28.
答案中的(E)顯然已提示甲、乙化合物是屬於某種異構物(分子式相同)，只是不是幾何異構。
一般而言，有機合成的產物指的是主要的化學反應產物，Reagent 的結果不可能認為是產物。
如烯與 $KMnO_{4(aq)}$ 在鹼中、低溫時，得乙二醇，通常不用寫出 $KMnO_4$ 變為何種東西。


(都是酯類)

參見附錄

33. CDE
有關催化劑的敘述，(E)選項"它無法改變反應產物的種類"，所指為特定反應中使用某一特定之催化劑，則反應產物的種類為固定。
倘若，一氧化碳與氫氣反應因使用不同催化劑形成不同產物，則不符合本題所述催化劑之定義。

38. ACE
(A)電極氧化(或還原)產生的電子(或電洞)會由外部電路流通，相對應的離子會經電解質流通。太陽能電池的電解質可參考文獻(Chem. Rev. vol. 95, pp49-68, 1995)圖 16 的例子。(如需參考文獻可來信索取)
(D)V=IR 的式子適用於不同的電池對同一電阻的情況。如用於一電阻，串連 2 個 1.5 V 電池所產生的電流會是 1 個 1.5 V 電池的兩倍。考慮一電池在放電的過程時，電池未釋放任何電流時有最高的電壓(即開路電壓)；而電池開始對外釋放電流時，電壓會下降，因為釋放電流的會損耗電極上的電子或電洞。故電壓下降而電流上升。

aldehyde + CF$_3$—C—OO$^-$ ⟶ **carboxylic acid** + CF$_3$—C—O$^-$

**ketone** + CF$_3$—C—OO$^-$ ⟶ **ester** + CF$_3$—C—O$^-$
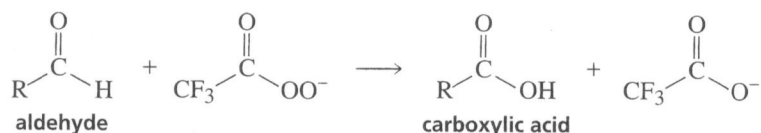
Aldehydes are oxidized to carboxylic acids by a peroxyacid.
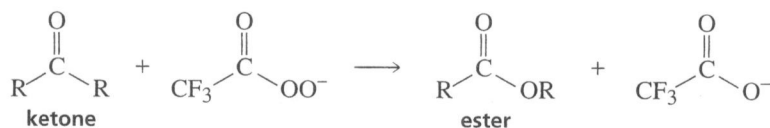
Ketones are oxidized to esters by a peroxyacid.

If the two alkyl substituents attached to the carbonyl group of the ketone are different, then on what side of the carbonyl carbon is the oxygen inserted? For example, does the oxidation of cyclohexyl methyl ketone form methyl cyclohexanecarboxylate or cyclohexyl acetate?

| cyclohexyl methyl ketone | methyl cyclohexanecarboxylate | cyclohexyl acetate |
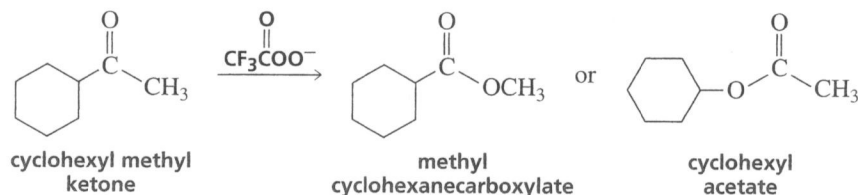
To answer this question, we need to look at the mechanism of the reaction.

MECHANISM FOR THE BAEYER–VILLIGER OXIDATION

a weak O—O bond

unstable intermediate
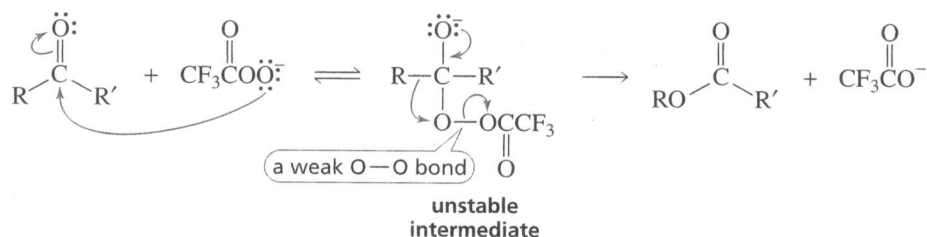
- The nucleophilic oxygen of the peroxyacid adds to the carbonyl carbon and forms an unstable tetrahedral intermediate with a weak O—O bond.
- As the π bond re-forms and the weak O—O bond breaks heterolytically, one of the alkyl groups migrates to an oxygen. This migration is similar to the 1,2-shifts that occur when carbocations rearrange (Section 6.7).

Studies of the migration tendencies of different groups have established the following order:

LEARN THE STRATEGY

relative migration tendencies

most likely to migrate ⟩ H > *tert*-alkyl > *sec*-alkyl ~ phenyl > primary alkyl > methyl ⟨ least likely to migrate

Therefore, the product of the Baeyer–Villiger oxidation of cyclohexyl methyl ketone is cyclohexyl acetate because a secondary alkyl group (the cyclohexyl group) is more likely to migrate than a methyl group. Aldehydes are always oxidized to carboxylic acids, because H has the greatest tendency to migrate.

PROBLEM 47 ◆

USE THE STRATEGY

What is the product of each of the following reactions?

a. (phenyl ketone) —CH$_2$CH$_3$ $\xrightarrow{CF_3COO^-}$

b. (benzaldehyde) —H $\xrightarrow{CF_3COO^-}$
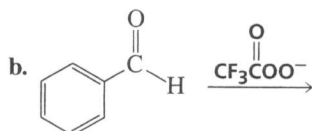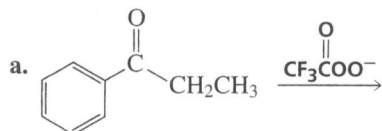
Light-Induced Redox Reactions in Nanocrystalline Systems

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Contents

1. Introduction

This review discusses salient features of interfacial electron transfer reactions in colloidal semiconductor solutions and thin films and their application for solar light energy conversion and photocatalytic water purification.[1] This research is interdisciplinary and is situated at the limit between colloid science, electrochemistry, and semiconductor physics. Sev-

eral intriguing features arise from the symbiosis of these areas of research. Colloidal science teaches us how to prepare very small semiconductor particles and how to stabilize these aggregates with respect to coagulation. Furthermore, it provides useful information on the surface thermodynamics of the colloid, e.g. electrostatic potential, acid base properties of surface hydroxyl groups, specific adsorption, electrolytic double layer properties, electrophoretic properties, etc. The electronic properties of the particles, on the other hand, relate to their solid state physics aspects, i.e. band structures and band gap, charge carrier mobilities and lifetimes, as well as the electrochemical positioning of the band edge potential with respect to the Nernst potential of the solution. Of particular importance are further quantum effects which arise when the size of the semiconductor particles becomes smaller than the Bohr radius of the first exciton state. Numerous important properties of the semiconductor, such as its optical absorption and luminescence emission, undergo drastic changes in this size domain.

A newly emerging research front which has given great impetus to the studies on colloidal semiconductors is that of heterogeneous photocatalysis. The size of the colloidal particles is generally small enough to render their solutions optically transparent allowing for convenient analysis of the elementary steps involved in the catalytic process. The use of time-resolved techniques such as laser photolysis will be described to derive the rate constant for electron–hole recombination within the TiO$_2$ particles and within nanocrystalline TiO$_2$ films of very high internal surface area. This technique has allowed the identification of the factors that govern the dynamics of interfacial electron and hole transfer reactions. Thus, the photocatalytic destruction of carbonaceous environmental pollutants in aqueous solutions comprises oxidation of the organic compound by valence band holes and this is coupled to the reduction of oxygen by conduction band electrons. Since the latter process occurs at a slow rate, it is often rate determining.[2] Therefore, to increase the efficiency of the TiO$_2$ photocatalysts, means have to be found to increase the rate of oxygen reduction. Judicious surface modification of the TiO$_2$, e.g. by chelating groups, was found to lead to a drastic acceleration of this important conduction band process.[3] Recent and very active research relates to the anchoring of charge transfer dyes to wide band gap semiconducting colloids rendering them sensitive to visible light.[4] Heterogeneous catalysts are frequently deposited onto the surface of the semiconductor to enhance multielectron transfer reactions such as the oxidation and reduction of water and this has received a great
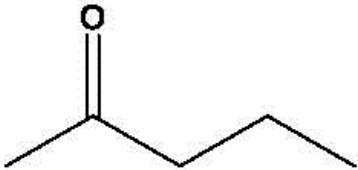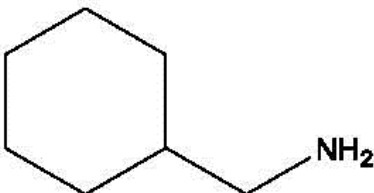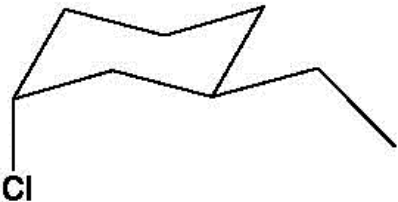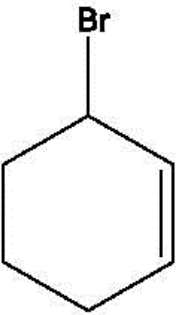
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國內初選筆試－非選擇題答案卷

三、非選擇題 (共 4 大題，每題 15 分)

1.	(1)	(2)
	(3)	(4)
	(5) d > c > a > b	

2.

(A)

k_1，d[B]/dt → 0 indicates [B] → 0; thus, $k_2 \gg k_1$

(B)

$$\frac{\mathrm{d}[\cdot CH_3]}{\mathrm{dt}} = k_a[CH_3CHO] - k_b[\cdot CH_3][CH_3CHO] + k_c[CH_3CO\cdot] - 2k_d[\cdot CH_3]^2 = 0$$

$$\frac{\mathrm{d}[CH_3CO\cdot]}{\mathrm{dt}} = k_b[\cdot CH_3][CH_3CHO] - k_c[CH_3CO\cdot] = 0$$

$$[\cdot CH_3] = (\frac{k_a}{2k_d})^{1/2}[CH_3CHO]^{1/2}$$

$$\frac{\mathrm{d}[CH_4]}{\mathrm{dt}} = k_b(\frac{k_a}{2k_d})^{1/2}[CH_3CHO]^{3/2}$$

$$級數 = \frac{3}{2}；反應速率常數 = k_b(\frac{k_a}{2k_d})^{1/2}$$

4

3.

14.95% Cr, 61.47% Ni, 23.54% Fe

$total: \quad 0.05177*50.00 - 5.49*0.06311 = 2.242 mmol$

$Fe + Ni: \quad 0.05168*36.28 = 1.875 mmol$

$Ni: \quad 0.05168*25.87 = 1.33696 mmol$

$Ni: \dfrac{1.33696*58.69/1000}{0.6382}*5*100\% = 61.47\%$

$Fe: \dfrac{(1.875-1.337)*55.847/1000}{0.6382}*5*100\% = 23.54\%$
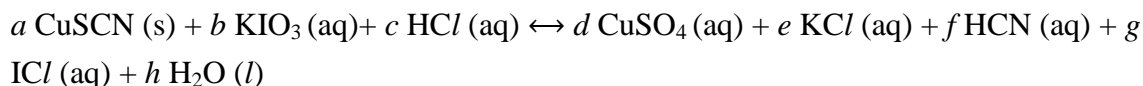
$Cr: \dfrac{(2.242-1.875)*51.996/1000}{0.6382}*5*100\% = 14.95\%$

說明：
乙二胺四醋酸(EDTA)濃度應一致為宜，唯敘述中以 0.05177M 或 0.05168M(相當接近)
作答皆不予以扣分。

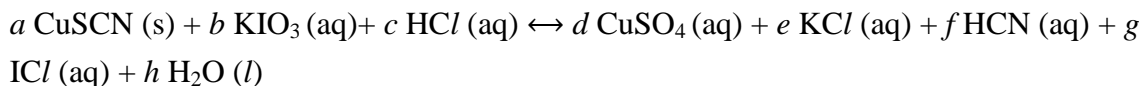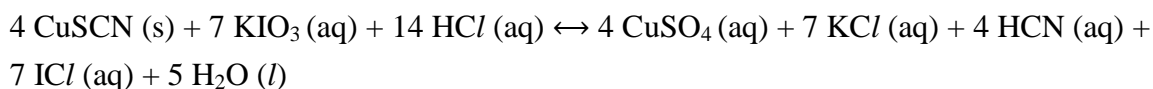|	
4.	某一未平衡化學方程式如下： a CuSCN (s) + b KIO$_3$ (aq)+ c HCl (aq) ↔ d CuSO$_4$ (aq) + e KCl (aq) + f HCN (aq) + g ICl (aq) + h H$_2$O (l) (A) 試問其平衡化學方程式中，$a \sim h$ 的值應該為何？(8 分) (B) CuSCN (s) 是一種配位聚合物，試問該聚合物中，與銅金屬鍵結的元素為何？(3 分) (C) 試問反應式右邊的產物中，何者具有顏色？(3 分) (D) ICl 分子中，I 的氧化態為何？(1 分) 備註：原題目 g ICl (aq)誤植為 g ICI (aq) **<u>解答</u>** 依答案細節，採部份給分 (A) 以下兩種解答皆可 (a-1) 若採 ICI (aq)作答 因為方程式左邊，C 與 N 比例為 $a / a = 1 / 1$；而在方程式右邊，C 與 N 比例為 $(f + g) / f \neq 1 / 1$。因 g 不可為 0，故以 ICI (aq)作答，此方程式無法平衡。 (a-2) 若採 ICl (aq)作答 a CuSCN (s) + b KIO$_3$ (aq)+ c HCl (aq) ↔ d CuSO$_4$ (aq) + e KCl (aq) + f HCN (aq) + g ICl (aq) + h H$_2$O (l) 平衡後，方程式如下 4 CuSCN (s) + 7 KIO$_3$ (aq) + 14 HCl (aq) ↔ 4 CuSO$_4$ (aq) + 7 KCl (aq) + 4 HCN (aq) + 7 ICl (aq) + 5 H$_2$O (l) (B) 與銅金屬鍵結的元素為 S 和 N (C) 藍色 CuSO$_4$ (aq) 、 紅棕色 ICl (aq) (D) ICl 分子中，I 的氧化態為 +1