

# 淡江大學八十八學年度碩士班招生考試試題

系別：化學學系

科目：分析化學

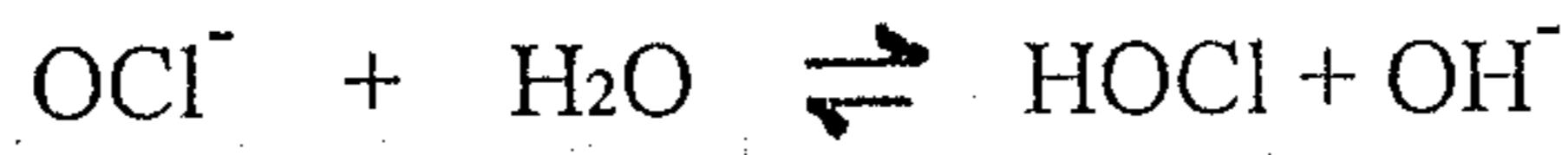
本試題共 3 頁

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1. Describe the preparation of 500 mL of 0.0740 M  $\text{Cl}^-$  solution from solid  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  (244.3 g/mol). (10%)

2. Calculate the hydroxide ion concentration in a 0.0100M sodium hypochlorite solution.

The equilibrium between  $\text{OCl}^-$  and water is



The acid dissociation constant for HOCl is  $3.0 \times 10^{-8}$ . (10 %)

3. Calculate the standard deviation of the result of

$$\frac{4.10(\pm 0.02) \times 0.0050(\pm 0.0001)}{1.97(\pm 0.04)} = 0.0104(\pm ?) \quad (10 \%)$$

4. Use activities to calculate the hydronium ion concentration in a 0.120M solution of  $\text{HNO}_2$  that is also 0.050M in NaCl. The acid dissociation constant for  $\text{HNO}_2$  is  $5.1 \times 10^{-4}$ . (10 %)

Activity Coefficients for Ions at 25°C\*

Ion	$\alpha_x, \text{nm}$	Activity Coefficient at Indicated Ionic Strength				
		0.001	0.005	0.01	0.05	0.1
$\text{H}_3\text{O}^+$	0.9	0.967	0.933	0.914	0.86	0.83
$\text{Li}^+, \text{C}_6\text{H}_5\text{COO}^-$	0.6	0.965	0.929	0.907	0.84	0.80
$\text{Na}^+, \text{IO}_3^-, \text{HSO}_3^-, \text{HCO}_3^-, \text{H}_2\text{PO}_4^-, \text{H}_2\text{AsO}_4^-, \text{OAc}^-$	0.4–0.45	0.964	0.928	0.902	0.82	0.78
$\text{OH}^-, \text{F}^-, \text{SCN}^-, \text{HS}^-, \text{ClO}_3^-, \text{ClO}_4^-, \text{BrO}_3^-, \text{IO}_4^-, \text{MnO}_4^-$	0.35	0.964	0.926	0.900	0.81	0.76
$\text{K}^+, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-, \text{NO}_2^-, \text{NO}_3^-, \text{HCOO}^-$	0.3	0.964	0.925	0.899	0.80	0.76
$\text{Rb}^+, \text{Cs}^+, \text{Ti}^+, \text{Ag}^+, \text{NH}_4^+$	0.25	0.964	0.924	0.898	0.80	0.75
$\text{Mg}^{2+}, \text{Be}^{2+}$	0.8	0.872	0.755	0.69	0.52	0.45
$\text{Ca}^{2+}, \text{Cu}^{2+}, \text{Zn}^{2+}, \text{Sn}^{2+}, \text{Mn}^{2+}, \text{Fe}^{2+}, \text{Ni}^{2+}, \text{Co}^{2+}, \text{Phthalate}^{2-}$	0.6	0.870	0.749	0.675	0.48	0.40
$\text{Sr}^{2+}, \text{Ba}^{2+}, \text{Cd}^{2+}, \text{Hg}^{2+}, \text{S}^{2-}$	0.5	0.868	0.744	0.67	0.46	0.38
$\text{Pb}^{2+}, \text{CO}_3^{2-}, \text{SO}_3^{2-}, \text{C}_2\text{O}_4^{2-}$	0.45	0.868	0.742	0.665	0.46	0.37
$\text{Hg}_2^{2+}, \text{SO}_4^{2-}, \text{S}_2\text{O}_3^{2-}, \text{CrO}_4^{2-}, \text{HPO}_4^{2-}$	0.40	0.867	0.740	0.660	0.44	0.36
$\text{Al}^{3+}, \text{Fe}^{3+}, \text{Cr}^{3+}, \text{La}^{3+}, \text{Ce}^{3+}$	0.9	0.738	0.54	0.44	0.24	0.18
$\text{PO}_4^{3-}, \text{Fe}(\text{CN})_6^{4-}$	0.4	0.725	0.50	0.40	0.16	0.095
$\text{Th}^{4+}, \text{Zr}^{4+}, \text{Ce}^{4+}, \text{Sn}^{4+}$	1.1	0.588	0.35	0.255	0.10	0.065
$\text{Fe}(\text{CN})_6^{4-}$	0.5	0.57	0.31	0.20	0.048	0.021

\*From J. Kielland, *J. Am. Chem. Soc.*, 1937, 59, 1675. By courtesy of the American Chemical Society.

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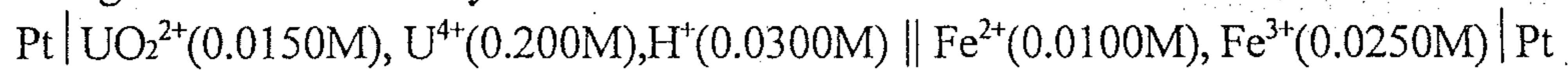
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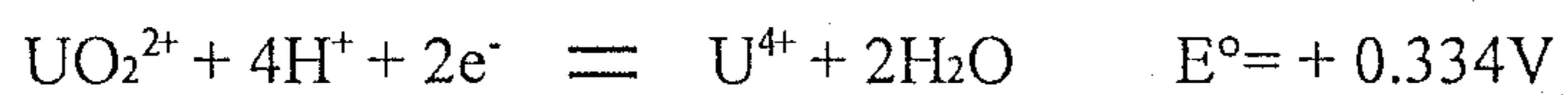
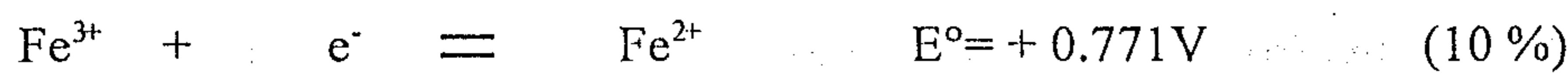
本試題共 3 頁

本試題雙面印刷

5. Calculate the thermodynamic potential of the following cell and indicate whether it is galvanic or electrolytic.



The two half-reactions are



6. Which of the following flames do you think will provide the most sensitive method for analysis by atomic emission spectroscopy?

- (a) Air-propane  
(b) Air-acetylene  
(c) Nitrous oxide-acetylene (5 %)

7. Suppose you are using a UV detector with a noise level of  $10^{-4}$  a.u. The detector is linear from the noise level to  $A=1$ , and a flow cell with a path length of 10 mm is used.

- (a) What is the linear range of the detector?  
(b) To calculate  $C_N$  (in  $\text{g cm}^{-3}$ ) for a solute with  $M_r = 100$  and absorptivity =  $1000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ . (10 %)

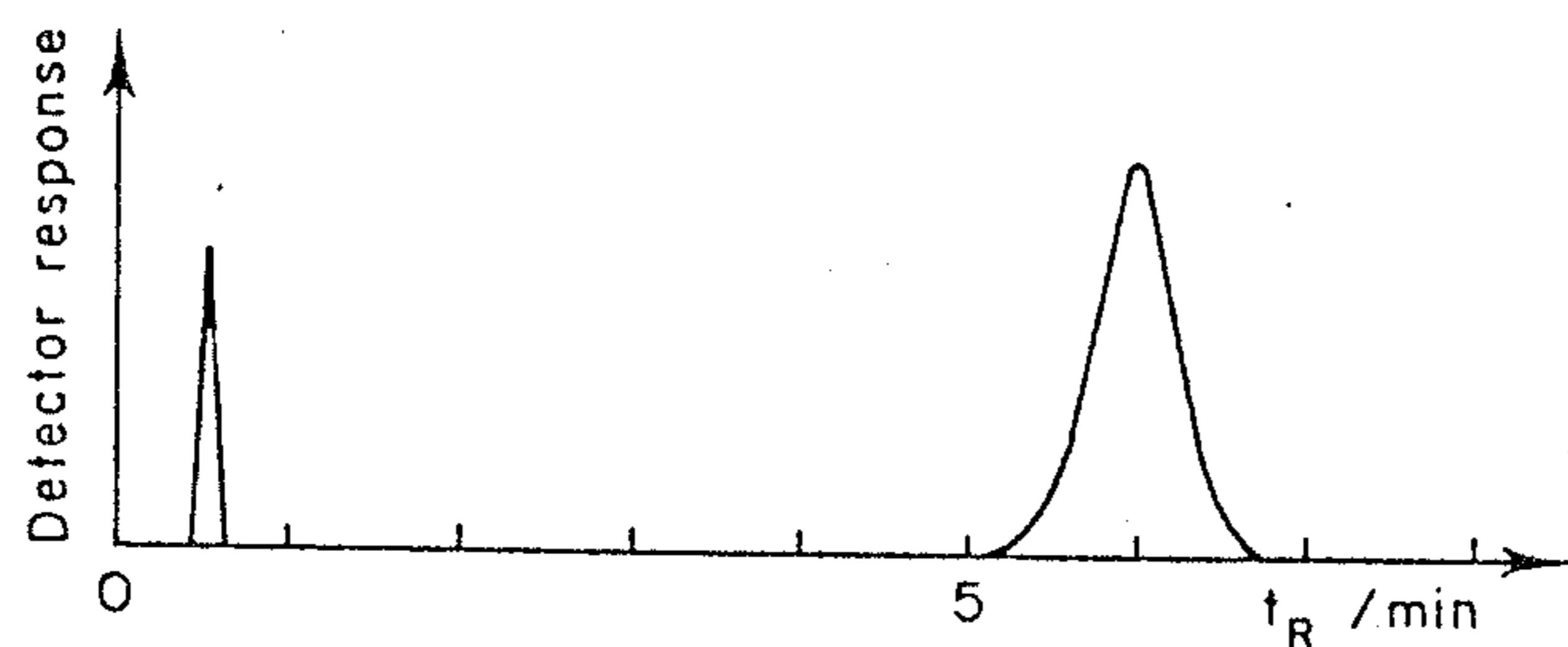
8. What is the effect of stationary-phase film thickness on gas chromatograms?

(5 %)

9. The following chromatogram was obtained from a 2 meter packed column.

Calculate the values of  $N$  and  $H$  for the second peak.

Note that the first peak is an unretained component. (10 %)



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本試題雙面印製

10. In a reversed-phase column, a solute was found to have a retention time of 31.3 min, while an unretained species required 0.48 min for elution when the mobile phase was 30% (by volume) methanol and 70% water. Calculate (a)  $k'$  and (b) a water/methanol composition that should bring  $k'$  to a value of about 5. (20%)

TABLE  
Properties of Common Chromatographic Mobile Phases

Solvent	Refractive Index <sup>a</sup>	Viscosity, cP <sup>b</sup>	Boiling Point, °C	Polarity Index, P'	Eluent Strength, ε <sup>c</sup>
Fluoroalkanes <sup>d</sup>	1.27–1.29	0.4–2.6	50–174	< -2	-0.25
Cyclohexane	1.423	0.90	81	0.04	-0.2
n-Hexane	1.372	0.30	69	0.1	0.01
l-Chlorobutane	1.400	0.42	78	1.0	0.26
Carbon tetrachloride	1.457	0.90	77	1.6	0.18
i-Propyl ether	1.365	0.38	68	2.4	0.28
Toluene	1.494	0.55	110	2.4	0.29
Diethyl ether	1.350	0.24	35	2.8	0.38
Tetrahydrofuran	1.405	0.46	66	4.0	0.57
Chloroform	1.443	0.53	61	4.1	0.40
Ethanol	1.359	1.08	78	4.3	0.88
Ethyl acetate	1.370	0.43	77	4.4	0.58
Dioxane	1.420	1.2	101	4.8	0.56
Methanol	1.326	0.54	65	5.1	0.95
Acetonitrile	1.341	0.34	82	5.8	0.65
Nitromethane	1.380	0.61	101	6.0	0.64
Ethylene glycol	1.431	16.5	182	6.9	1.11
Water	1.333	0.89	100	10.2	Large

<sup>a</sup> At 25°C.

<sup>b</sup> The centipoise is a common unit of viscosity; in SI units, 1 cP = 1 mN · s · m<sup>-2</sup>.

<sup>c</sup> On Al<sub>2</sub>O<sub>3</sub>. Multiplication by 0.8 gives ε<sup>d</sup> on SiO<sub>2</sub>.

<sup>d</sup> Properties depend upon molecular weight. Range of data given.