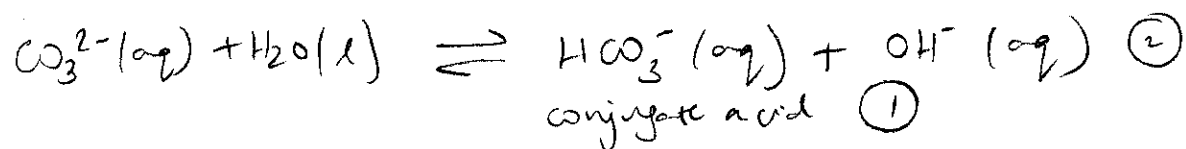1) Write the proton transfer equilibria reaction in aqueous solution for the following bases and identify the conjugate acids of each

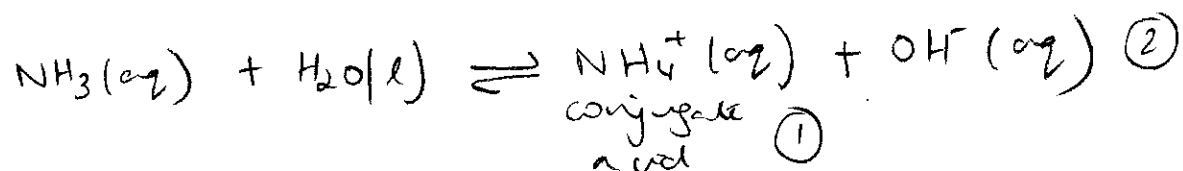1 a) CO_3^{2-} (3 points)

$$CO_3^{2-}(aq) + H_2O(l) \rightleftharpoons HCO_3^-(aq) + OH^-(aq) \quad ②$$

conjugate acid ①

1 b) Ammonia, NH_3 (3 points)

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq) \quad ②$$

conjugate acid ①

1c) If K_b for ammonia is 1.8×10^{-5}, calculate K_a for its conjugate acid   (3 points)
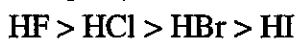
$$K_a(NH_4^+(aq)) = \frac{K_w}{K_b(NH_3(aq))} \quad ②$$

$$= \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} \quad ①$$

2) Briefly explain the trend in acid strength observed in aqueous solutions of the halogen acids

HI(aq) > HBr(aq) > HCl(aq) > HF(aq);   HI(aq) (hydroiodic acid) is the strongest of the halogen acids, HF(aq) (hydrofluoric acid) the weakest. The trend in bond dissociation energy is

HF > HCl > HBr > HI   (6 points)
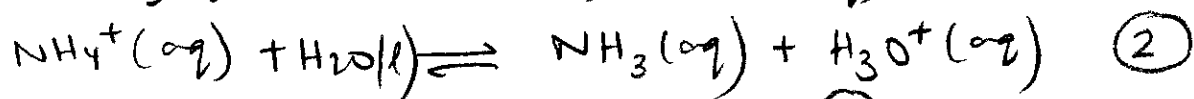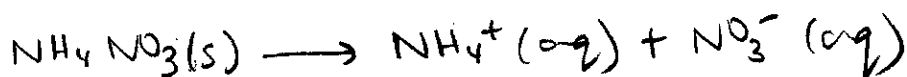
Strength of acid depends on ease with which it gives up a proton. As bond strength decreases ease with which the molecule donates a H^+ is easier. H-I with the weakest bond amongst the halogen acids, is therefore the strongest amongst the halogen acids.

3) Determine whether aqueous solutions of the following ionic compounds have a pH equal to, greater than, or less than 7. Assume each compound is highly soluble in water. **Write a chemical equation for the dissolution of each in water. If the pH will be greater than 7 or less than 7, write a chemical reaction which justifies your answer. If the pH = 7 explain why.**

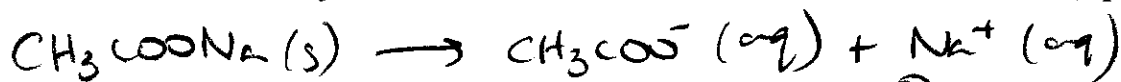3a) Ammonium nitrate, NH_4NO_3 (5 points)

$$NH_4NO_3(s) \longrightarrow NH_4^+(aq) + NO_3^-(aq)$$
$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_3(aq) + H_3O^+(aq) \quad ②$$
$$NO_3^-(aq) \text{ is a neutral anion. } ①$$
$$pH < 7 \text{ because of hydrolysis of } NH_4^+(aq) ②$$

3b) Sodium acetate, CH_3COONa (5 points)

$$CH_3COONa(s) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$$
$$Na^+(aq) \text{ is a neutral cation } ①$$
$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq) ②$$
$$pH > 7 \quad ②$$

3
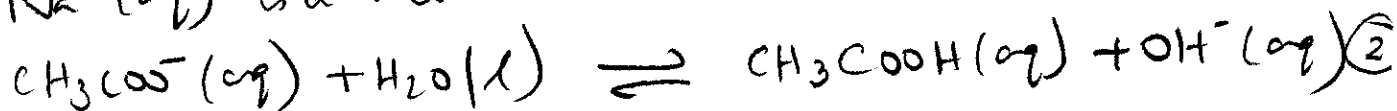
3c) Potassium chloride, KCl   (5 points)

$$KCl(s) \longrightarrow K^+(aq) + Cl^-(aq)$$

Both $K^+(aq)$ and $Cl^-(aq)$ are neutral ions, ③
do not hydrolyze

pH = 7   ②

4) A 25.0 mL sample of 0.10 M $CH_3COOH(aq)$ is titrated with 0.10 M NaOH(aq). K_a (CH_3COOH) at 25°C = 1.8 x 10^{-5}. **For each question below, show all chemical equations relevant to solving the problem. Also show all calculations in support your answer. Credit will not be given unless you clearly show how you came to your answer.**

4a) What is the initial pH of the 0.10 M $CH_3COOH(aq)$ solution?   (6 points)

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq) ②$$
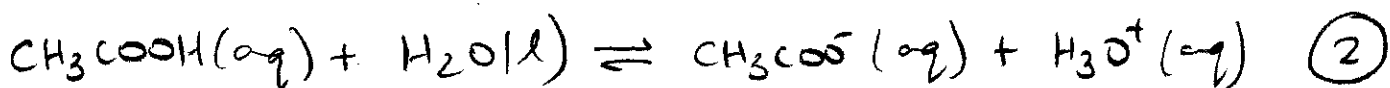
	$[CH_3COOH(aq)]$	$[CH_3COO^-(aq)]$	$(H_3O^+(aq))$
Initial	0.10	0	0
change	-x	x	x
Equilibrium	0.10 - x	x	x

$$\frac{x^2}{0.10-x} = 1.8 \times 10^{-5} ②$$

Assume $x \ll 0.10$ $x = 1.3 \times 10^{-3}$ M. ①

pH = 2.87   ①

4

4b) What is the pH after the addition of 10.0 mL of 0.10 M NaOH(aq)?   (9 points)

Addition of OH^- to CH_3COOH

$$OH^-(aq) + CH_3COOH(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l) \quad ②$$
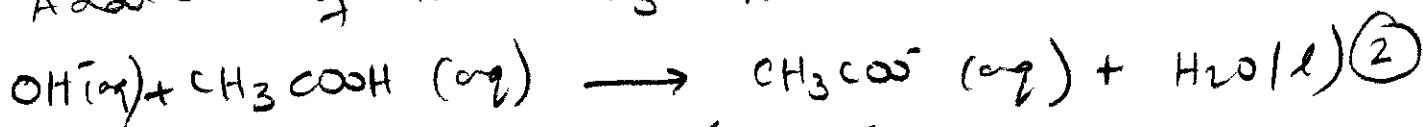
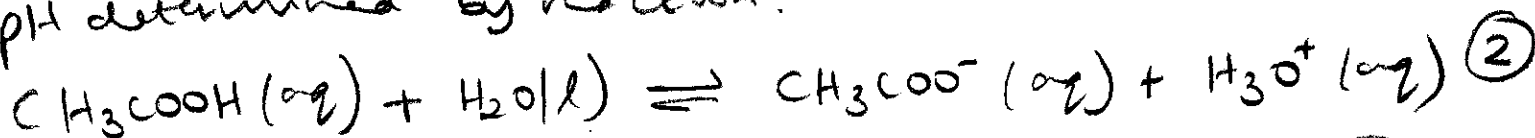Forms a buffer CH_3COOH/CH_3COO^-

Mols of OH^- added $= 0.0010$ mols

Mols of CH_3COO^- formed $= 0.0010$ mols

Mols of CH_3COOH unreacted $= 0.0025 - 0.0010 = 0.0015$ mols ①

Concentration of $CH_3COOH = \dfrac{0.0015 \text{ mols}}{0.0250L + 0.0100L} = 4.3 \times 10^{-2} M$ ①

concentration of $CH_3COO^- = \dfrac{0.0010 \text{ mols}}{0.0350 L} = 2.8 \times 10^{-2} M$ ①

pH determined by reaction:

$$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq) \quad ②$$

	$[CH_3COOH(aq)]$	$[CH_3COO^-(aq)]$	$[H_3O^+(aq)]$
initial	$4.3 \times 10^{-2} M$	$2.8 \times 10^{-2} M$	0
change	$-x$	x	x
Equilibrium	$4.3 \times 10^{-2} - x$	$2.8 \times 10^{-2} + x$	x

②

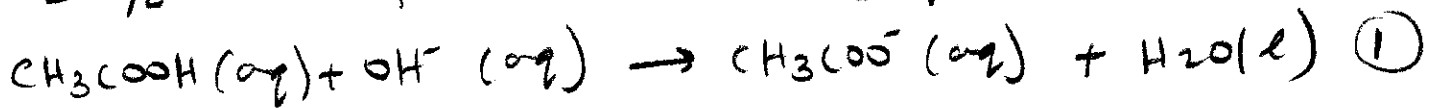$$\frac{x(2.8 \times 10^{-2} + x)}{4.3 \times 10^{-2} - x} = 1.8 \times 10^{-5} \qquad \text{Assume } x \ll 2.8 \times 10^{-2}$$

$$x = 2.7 \times 10^{-5} M$$

$$pH = 4.56 \quad ①$$

4c) What volume of 0.10 M NaOH(aq) is required to reach halfway to the equivalence point?

Halfway point reached when mols of OH⁻ added ⎤ ②
= ½ mols of CH_3COOH initially present. ⎦
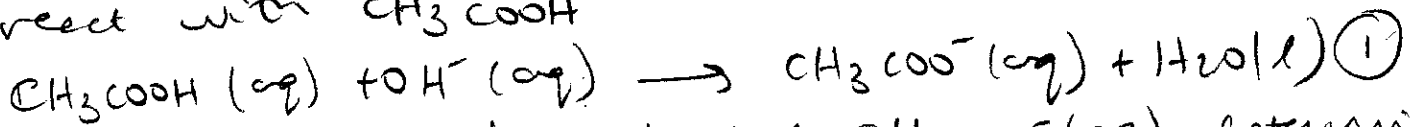
$CH_3COOH (aq) + OH^- (aq) \rightarrow CH_3COO^- (aq) + H_2O(l)$ ①

initial number of mols of CH_3COOH = 0.0025 mols

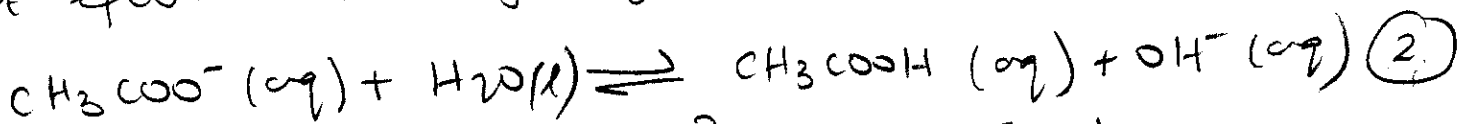Number of mols of OH⁻ added at halfway = 0.00125 mols ⎤
Need 12.5 ml of 0.10 M NaOH to reach halfway point. ⎦ ②

4d) Calculate the pH at the equivalence point. (9 points)

At equivalence point enough OH⁻ added to completely react with CH_3COOH

$CH_3COOH (aq) + OH^- (aq) \rightarrow CH_3COO^- (aq) + H_2O(l)$ ①

At equivalence hydrolysis of $CH_3COO^- (aq)$ determines pH

$CH_3COO^- (aq) + H_2O(l) \rightleftharpoons CH_3COOH (aq) + OH^- (aq)$ ②

At equivalence $[CH_3COO^- (aq)] = \dfrac{0.0025 \text{ mols}}{0.0250L + 0.0250L} = 0.050 M$ ①

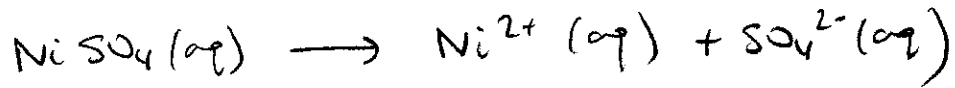|	$[CH_3COO^-]$	$[CH_3COOH]$	$[OH^-]$	
initial	0.050	0	0	②
change	$-x$	x	x	
equil.	$0.050-x$	x	x	

$\dfrac{x^2}{0.050-x} = \dfrac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$
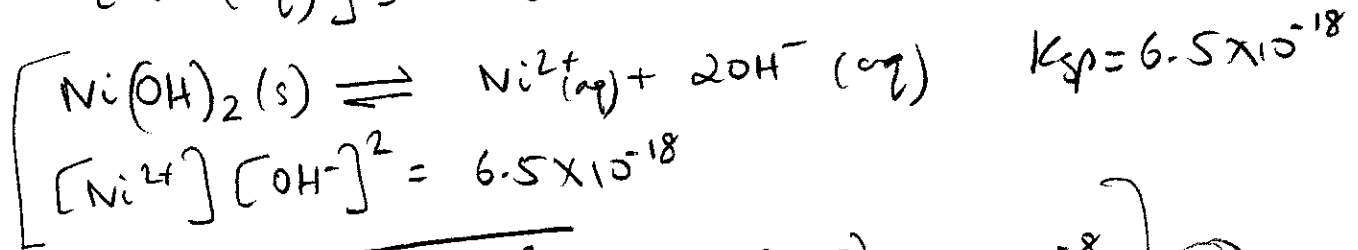
Assume $x << 0.050$ $x = 5.27 \times 10^{-6} M$

pOH = 5.28 ①

$\boxed{pH = 8.72}$ ②

6

5) Determine the pH required for the onset of precipitation of $Ni(OH)_2(s)$ from a 0.060 M $NiSO_4(aq)$ solution. (6 points)

$$Ni SO_4 (aq) \longrightarrow Ni^{2+}(aq) + SO_4^{2-}(aq)$$

① $[Ni^{2+}(aq)] = 0.060 \ M$

② $\left[\begin{array}{l} Ni(OH)_2(s) \rightleftharpoons Ni^{2+}(aq) + 2OH^-(aq) \quad K_{sp} = 6.5 \times 10^{-18} \\ [Ni^{2+}][OH^-]^2 = 6.5 \times 10^{-18} \end{array}\right.$

$[OH^-] = \sqrt{\dfrac{6.5 \times 10^{-18}}{0.060}}$

$[OH^-] = 1.0 \times 10^{-8}$
pOH = 8 ②

$\boxed{pH = 6}$ ①

6) Which anion fluoride (F^-) or carbonate (CO_3^{2-}), would be a better choice for separating Ba^{2+} ions from Ca^{2+} ions from an aqueous solution containing both ions? Briefly explain your choice of anion. Also predict which salt would precipitate first on addition of the anion you decide is better for separating the two cations. (7 points)
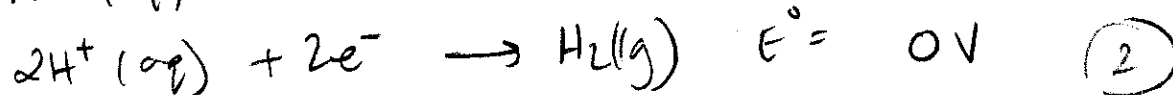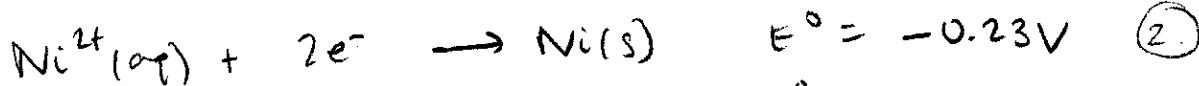
	K_{sp}		K_{sp}
BaF_2	1.7×10^{-6}	CaF_2	4.0×10^{-11}
$BaCO_3$	8.1×10^{-9}	$CaCO_3$	8.7×10^{-9}
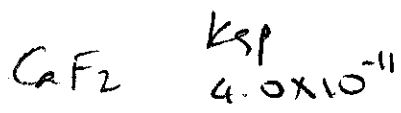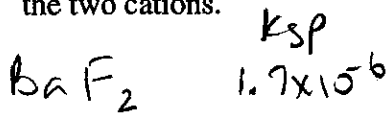
K_{sp} ↓ BaF_2 and CaF_2 differ by ~ 5 orders of magnitude
K_{sp} ↓ $BaCO_3$ and $CaCO_3$ very similar
F^- is a better choice to separate Ba^{2+} & Ca^{2+}
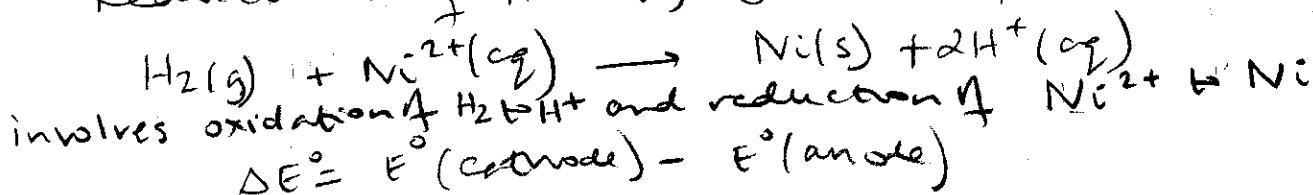If F^- added expect CaF_2 to precipitate first

7

7) Answer the following questions. **For each YES response write a balanced overall balanced cell reaction and calculate the standard cell potential. For a NO answer briefly explain why your answer is no.**

7 a) Can H_2 **reduce** Ni^{2+}(aq) ions to nickel metal?   (10 points)

$$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s) \qquad E^\circ = -0.23V \quad ②$$

$$2H^+(aq) + 2e^- \longrightarrow H_2(g) \qquad E^\circ = 0V \quad ②$$

Reduction of $Ni^{2+}(aq)$ by H_2 is the following reaction

$$H_2(g) + Ni^{2+}(aq) \longrightarrow Ni(s) + 2H^+(aq)$$

involves oxidation of H_2 to H^+ and reduction of Ni^{2+} to Ni

$$\Delta E^\circ = E^\circ(cathode) - E^\circ(anode)$$

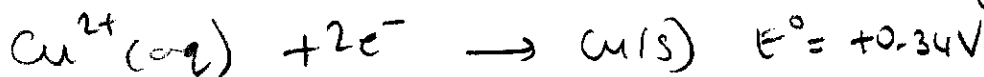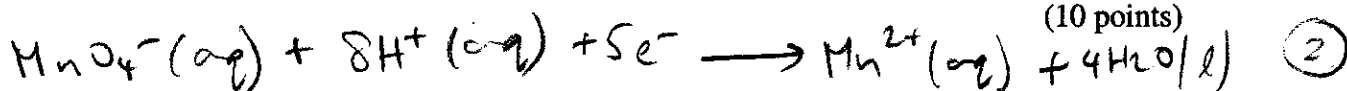$$= E^\circ_{Ni^{2+}/Ni} - E^\circ_{H^+/H_2}$$

$$= -0.23V - 0 = -0.23V$$

Since $\Delta E^\circ < 0$ reaction is not spontaneous
hence H_2 cannot reduce Ni^{2+} ⑥

7 b) Can permanganate ions (MnO_4^-) ions **oxidize** copper metal to Cu^{2+} (aq) ions in an acidic solution?
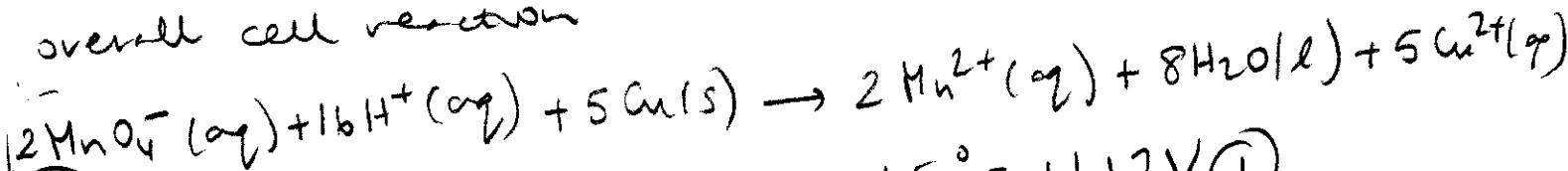(10 points)

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l) \quad ②$$

$$E^\circ = +1.51V$$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad E^\circ = +0.34V \quad ②$$

$MnO_4^-(aq)$ in acidic solution can oxidize $Cu(s)$ to Cu^{2+} ②
overall cell reaction

$$2MnO_4^-(aq) + 16H^+(aq) + 5Cu(s) \longrightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5Cu^{2+}(aq)$$
③

$$\Delta E^\circ = +1.17V ①$$

8

8) Determine the cell voltage for the following galvanic cell at 25°C
Cr(s) | Cr^{3+} (aq, 0.37 mol/L) || Pb^{2+}(aq, 9.5 x 10^{-3} mol/L) | Pb(s)   (8 points)
Write a balanced overall cell reaction for this cell.
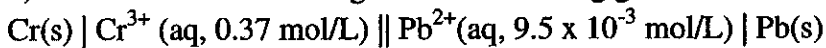
Anode $Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$

Cathode $Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$

Overall cell reaction

$2Cr(s) + 3Pb^{2+}(aq) \longrightarrow 3Pb(s) + 2Cr^{3+}(aq)$ (2)
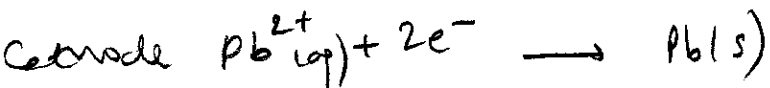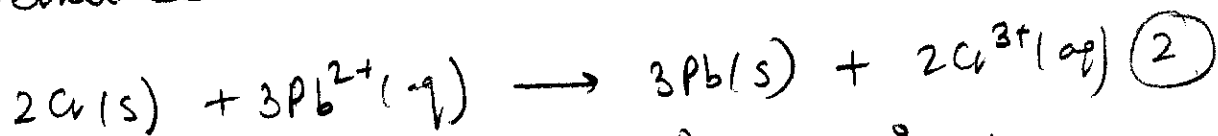
$$\Delta E° = E°_{Pb^{2+}/Pb} - E°_{Cr^{3+}/Cr}$$
$$= -0.13V - (-0.74V)$$
$$= +0.61V \quad (2)$$

$$\Delta E = \Delta E° - \frac{RT}{nF} \ln Q$$

$$= 0.61 - \frac{0.02569}{6} \ln \frac{[Cr^{3+}(aq)]^2}{[Pb^{2+}(aq)]^3} \quad (3)$$

$$= 0.61 - \frac{0.02569}{6} \ln \frac{(0.37)^2}{(9.5 \times 10^{-3})^3}$$

$$\boxed{\Delta E = 0.56V} \quad (1)$$

9