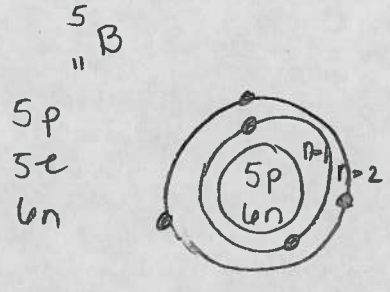
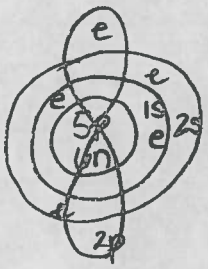
Unit 1

1a) Bohr vs Quantum $1s^2 2s^2 2p^1$ similarities





nucleus - center of atom
- contains p + n.
- n = energy level.

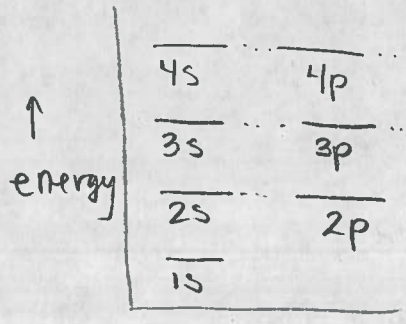
- all energy levels have a set path around nucleus
- all e⁻'s travel on path
- 2 e⁻'s on n=1
- 8 e⁻'s on n=2, n=3

n=1 - 1 type of orbital s
n=2 l=0,1 . s+p orbitals
n=3 l=0,1,2 - s, p, d - orb.
n=4 l=0,1,2,3 - s, p, d, f orb
* only 2 e⁻'s per orbital

* energy levels are quantized - orbitals are quantized.
ie no e⁻'s exist b/w orbitals

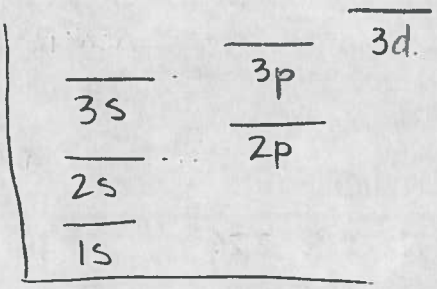
orbitals - regions of space in which e⁻ is found in 95% certainty
- s - orbital (1 type) - sphere shape
- p - orbital (3) - dumbbell
- d - orb (5)
- f - orb (7)
- e⁻'s in same orbital have opposite spins

b) 1 e⁻ system



* orbitals in same energy level have same amt of E
∴ if e⁻ falls from 4s, 4p or 4d will produce same colour of light

multi e⁻ system

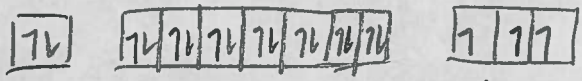


* orbitals w same n value have different amts of energy
∴ when e⁻ falls from 3s, 3p, 3d 3 different colours would be prod
- colour corresponds to energy value

2. Bismuth - element 83

a) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 6p^3$

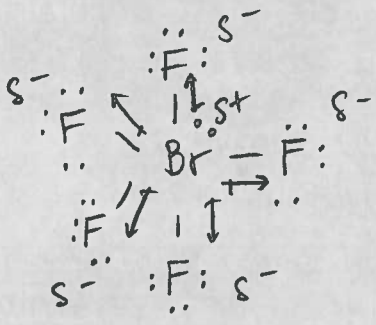
b) $[Xe]\ 6s^2\ 4f^{14}\ 6p^3$

c) $[Xe]$ 

d) $n = 6 \quad l = 1 \quad m_l = -1 \quad m_s = +\frac{1}{2}$

3 a) BrF_5 (2.96, 3.98) $\Delta EN = 1.02$

$6 \times 7 = 42$



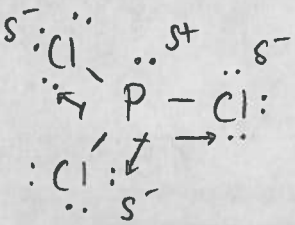
square pyramidal
- Polar
- dipole-dipole

b) PCl_3 (2.19, 3.16) $\Delta EN = 0.97$

3×7

$+5$

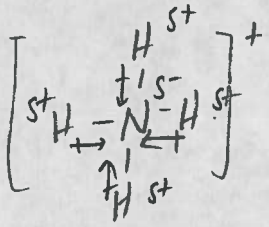
$= 26$



trigonal pyramidal
- Polar
- Dip-dip

c) NH_4^+ (3.04, 2.20)

$5 \quad 4 - 1 = 8$

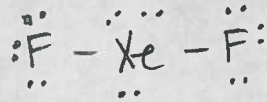


tetrahedral
- NP
- Disp F.
- overall + molecule
- ionic.

d) XeF_2 (3.98)

$8 + 2(7)$

$= 22$



- linear
NP
- forces would cancel.
- Disp F

4 HF vs HCl, HBr, HI

$\Delta EN = 0.96$ ↘ $\Delta EN = 0.76$ ↘ $\Delta EN = 0.46$

* bond becomes less + less polar

HF - H-bond.

HCl, HBr, HI - dipole-dipole - but this interm F decreases as ΔEN lowers.

H bonded to N, O, F

H-bond

< extreme dip-dip

hydrogen bonding

$\Delta EN = 3.98 - 2.20$

$= 1.78$

* borderline polar covalent / ionic

5a) $CH_3CH_2CH=CHCH_3 + I_2 \rightarrow CH_3-CH_2CH(I)-CH(I)-CH_3$

2-pentene
alkene
- disp F
- Addn.

2,3-diiodopentane
(dipole-dipole

b) $CH_3CH_2CH_2-OH + HCl \rightarrow CH_3CH_2-CH_2-Cl + HOH$

- 1-propanol
- alcohol (1°)
- H-bond
- substitn

1-chloropropane

c) $CH_3CH(CH_3)-C(=O)H \xrightarrow{[O]} CH_3-CH(CH_3)-C(=O)-OH$

2-methylpropanal
- dipole-dipole
- aldehyde
- oxidatn

2-methylpropanoic acid.

d) $CH_3CH_2-CH_2-OH + H-C(=O)-OH \rightarrow CH_3-CH_2-CH_2-O-C(=O)-H + H_2O$

alcohol (1°)
- H-bond
- condensatn rxn

c. acid.
- H-bond.

methyl propanoate
- ester.

e) $C-C-C-C-C-C-C(OH) \xrightarrow[\Delta]{H_2SO_4} C-C-C-C-C-C=C + H_2O$

alcohol (1°)
- H-bond.
- elimination rxn

heptene.
- disp F

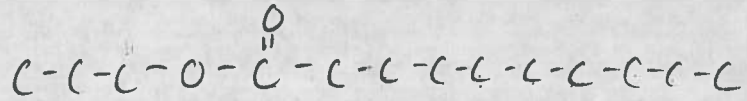
f) $CH_2=CHCH_3 + H_2O \rightarrow CH_3-CH(OH)-CH_3 + CH_2(OH)-CH_2-CH_3$

- propene
- disp F
- Addn rxn

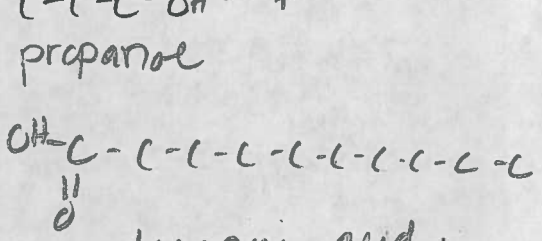
major

minor

(Markovnikov Rule)

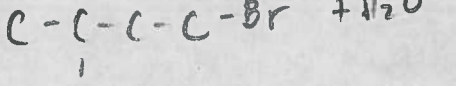
g) 

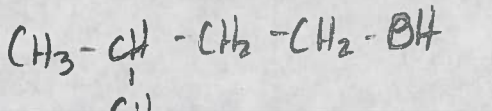
- ester
- dip-dip
- hydrolysis rxn



propanol

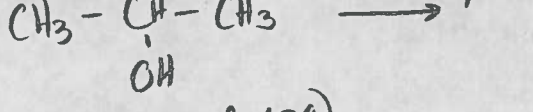
decanoic acid.

h 



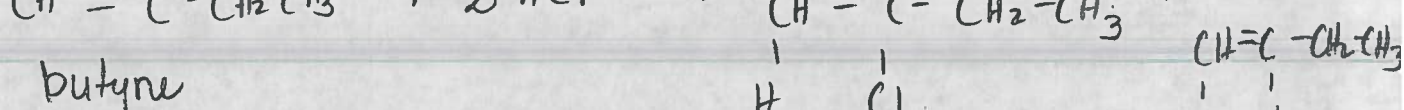
1-bromo-3-methylbutane
- dip-dip
- substitn

3-methyl-butanol.

i) 

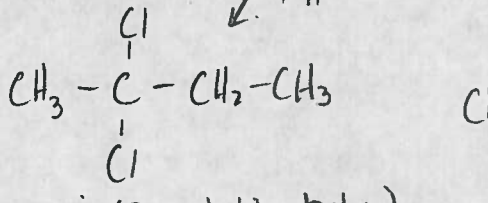
2-propanol (2°)
- H-bond alcohol
- oxidatn (purple)

Ketone
2-propanone (brown)

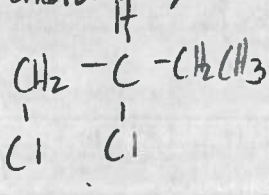
j) 

butyne
- alkyne
- diap F
- Addn rxn

major



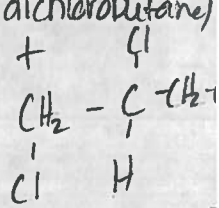
major (2,2-dichlorobutane)



minor (1,2-dichlorobutane)

minor

(1,1-dichlorobutane)



(1,2-dichlorobutane)

6. 2.5g NH_4Cl

130 ml H_2O

$T_i = 21°C$

$T_f = 16.6°C$

$\Delta T = 16.6 - 21$

$= -4.4°C$

$Q_{soln} = mc\Delta T$

$= (130g)(4.184 J/g°C)(-4.4°C)$

$= -2393.248 J$

$Q_{rxn} = -Q_{soln}$

$= +2393.248 J$

$n_{NH_4Cl} = \frac{m}{m}$

$= \frac{2.5g}{53.4917 g/mol}$

$= 0.0467 mol.$

$\Delta H_{rxn} = \frac{Q_{rxn}}{n}$

$= \frac{+2393.248 J}{.0467 mol}$

$= +51207.62 J$

$= +51.2 KJ/mol$

7. 110mL

0.3M $Mg(OH)_2$

95mL

0.4M HCl

$\Delta T = +8.8°C$

$V_T = 110 + 95$

$= 205 mL$

$Mg(OH)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O$

$V = 110mL$ $V = 95mL$

$C = 0.3M$ $C = 0.4M$

$n = CxV$ $n = CxV$

$= (.3)(.110)$ $= (.4)(.095)$

$= 0.033$ $= 0.038 mol$

mol ratio 1:2

$\frac{1 mol}{2} = \frac{0.033 mol}{x}$

$x = 0.0165 mol \therefore$ LR HCl.

$Q_{soln} = m_{soln} c\Delta T$

$= (205)(4.184)(8.8)$

$= +7547.94 J$

$Q_{rxn} = -Q_{soln}$

$= -7547.94 J$

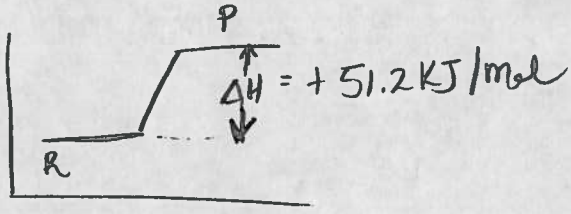
$\Delta H_{rxn} = \frac{Q_{rxn}}{n}$

$= \frac{-7547.94 J}{0.038 mol}$

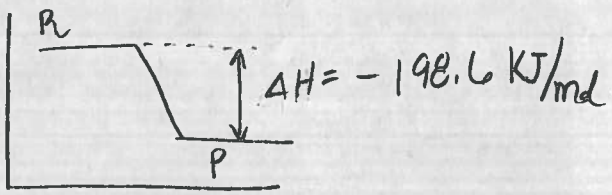
$= -198629.8 J/mol$

$= -198.6 KJ/mol$

8. Q #6



Q7.



9. $CH_4 + NH_3 \rightarrow HCN + 3H_2$

÷2 (1) $H_2 + 2C + N_2 \rightarrow 2HCN \quad \Delta H^\circ = 270$

rev ÷2. (2) $N_2 + 3H_2 \rightarrow 2NH_3 \quad \Delta H^\circ = -92.$

rev (3) $C + 2H_2 \rightarrow CH_4 \quad \Delta H^\circ = -75\ KJ$

(2) $NH_3 \rightarrow \frac{1}{2}N_2 + \frac{3}{2}H_2 \quad \Delta H = +46.\ KJ$

(3) $CH_4 \rightarrow C + 2H_2 \quad \Delta H = +75\ KJ$

(1) $\frac{1}{2}H_2 + C + \frac{1}{2}N_2 \rightarrow HCN \quad \Delta H = +135$

$NH_3 + CH_4 \rightarrow 3H_2 + HCN \quad \Delta H = +256\ KJ$

10.

$[HgCl_2]$	$[C_2O_4^{2-}]$	
.0788	.113	1.35×10^{-6}
.0788 (x2)	.225	5.33×10^{-6}
.039	.225	2.63×10^{-6}

(x2 between rows 1 and 2; x4 between rows 1 and 3; x2 between rows 2 and 3)

rate $\propto [HgCl_2]$: $2 = 2^x$, $x = 1$

rate $\propto [C_2O_4^{2-}]$: $4 = 2^y$, $y = 2$

∴ a) rate $= k[HgCl_2][C_2O_4^{2-}]^2$

$k = \frac{\text{rate}}{[HgCl_2][C_2O_4^{2-}]^2}$

$= \frac{1.35 \times 10^{-6}}{(.0788)(.113)^2}$

b) $= 0.00134\ L^2/mol^2 \cdot s$

c) rate $= (.00134)(.04)(.15)^2$

$= 1.206 \times 10^{-6}\ mol/L \cdot s$

11. $O_3 + NO \rightleftharpoons NO_2 + O_2 \quad K_{eq} = 6.70$

$[R] = \frac{n}{V}$

$= \frac{1.92 \text{ mol}}{2.0 \text{ L}}$

$= 0.96 \text{ M}$

	O_3	NO	NO_2	O_2
I	0.96	0.96	—	—
C	$-x$	$-x$	$+x$	$+x$
E	$0.96-x$	$.96-x$	$+x$	$+x$

@ equilm
$[NO_2] = [O_2]$
$= 0.69 \text{M}$

$[O_3] = [NO]$
$= .96 - x$
$= .96 - .69$
$= 0.27 \text{M}$

$K_{eq} = \frac{[NO_2][O_2]}{[O_3][NO]}$

$6.70 = \frac{(x)^2}{(.96-x)^2}$

$\sqrt{6.70} = \sqrt{\frac{x^2}{(.96-x)^2}}$

$2.588 = \frac{x}{.96-x}$

$(2.588)(.96-x) = x$

$2.48 - 2.588x = x$

$\frac{2.48}{3.58} = \frac{3.58x}{3.58}$

$x = 0.69$

12. $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^- \quad K_b = 4.6 \times 10^{-4}$

	CH_3NH_2	H_2O	$CH_3NH_3^+$	OH^-
I	1.75		—	—
C	$-x$		$+x$	$+x$
E	$1.75-x$		$+x$	$+x$

$K_b = \frac{[CH_3NH_3^+][OH^-]}{[CH_3NH_2]}$

$4.6 \times 10^{-4} = \frac{(x)(x)}{1.75-x}$

$x \ll 1.75$

$x = \sqrt{(1.75)(4.6 \times 10^{-4})}$

$x = 0.028$

$\therefore [OH^-] = x = 0.028$

$pOH = -\log[OH^-]$

$= 1.55$

$\therefore pH = 14 - pOH$

$= 12.45$

% dissociation

$\frac{[OH]}{[Base]} \times 100$

$= \frac{.028}{1.75} \times 100$

$= 1.6\%$

13. weak acid $C_6H_5NH_2$ + strong base HBr $\rightarrow$ $C_6H_5NH_3Br$

$V = 112.5\,mL$ $C = 0.075M$ $\quad$ $0.075M$

$C_6H_5NH_3Br$: reacts w/ H_2O; NR w/ H_2O

$\therefore$ neutralize 1:1 ratio

use 112.5 mL HBr.

$n = CV$

$= (.075)(.1125)$

$= 0.00843\,mol$

$\therefore$ n salt $C_6H_5NH_3Br$

$= 0.00843\,mol$

$[C_6H_5NH_3Br] = \frac{n}{V}$

$= \frac{.00843\,mol}{(.225\,L)}$

$= 0.0375M$

$\therefore$

	$C_6H_5NH_3^+$	+ H_2O $\rightleftharpoons$	$C_6H_5NH_2$	+ H_3O^+
I	0.0375		—	—
C	$-x$		$+x$	$+x$
E	$.0375-x$		$+x$	$+x$

$K_a * K_b = K_w$

$K_a = \frac{K_w}{K_b}$

$= \frac{1.0 \times 10^{-14}}{7.4 \times 10^{-10}}$

$= 1.35 \times 10^{-5}$

$K_a = \frac{[H_3O^+][C_6H_5NH_2]}{[C_6H_5NH_3^+]}$

$1.35 \times 10^{-5} = \frac{(x^2)}{.0375-x}$

$x \ll .375$

$x = \sqrt{(.0375)(1.35 \times 10^{-5})}$

$= 0.000711$

$x = [H_3O^+]$

$= 0.000711$

$pH = -\log[H_3O^+]$

$= -\log(.000711)$

$= 3.15$ ✓

14

weak base + strong acid → N_2H_5Br (reacts with H_2O)

$K_b = 7.94 \times 10^{-9}$

N_2H_4	HBr	N_2H_5Br
60 mL	C = 0.2 M	
0.1 M	V = ?	

$n = C \times V$

$= (.1)(.06)$

$= 0.006$ mol

1:1 ratio

$C = \frac{n}{V}$

$V = \frac{n}{C}$

$= \frac{.006 \text{ mol}}{0.2 \text{ mol/L}}$

$= 0.03$ L

1:1:1

$\therefore n\ N_2H_5Br = 0.006$ mol

$V_T = 0.03 + 0.06$

$= 0.09$ L

$\therefore [N_2H_5Br] = \frac{n}{V}$

$= \frac{0.006}{0.09}$

$= 0.0666$ M

	$N_2H_5^+$	+ H_2O ⇌	N_2H_4	+ H_3O^+
I	.066	—	—	—
C	−x		+x	+x
E	0.066−x		+x	+x

$K_a = \frac{K_w}{K_b}$

$= \frac{1.0 \times 10^{-14}}{7.94 \times 10^{-9}}$

$= 1.259 \times 10^{-6}$

$K_a = \frac{[N_2H_4][H_3O^+]}{[N_2H_5^+]}$

$1.259 \times 10^{-6} = \frac{x^2}{(0.066 - x)}$

$x << .066$

$x = \sqrt{(.066)(1.259 \times 10^{-6})}$

$= 0.000288$

$\therefore [H_3O^+] = x$

$= .000288$

$pH = -\log[H_3O^+]$

$= -\log(.000288)$

$= 3.54$ ✓

15 a) $Ag_2CO_{3(s)} \rightleftharpoons 2Ag^+ + CO_3^{2-}$

b) $Y(IO_3)_{3(s)} \rightleftharpoons Y^{3+} + 3IO_3^-$

c) $Cu_3(PO_4)_{2(s)} \rightleftharpoons 3Cu^{2+} + 2PO_4^{3-}$

16 a)

$$Y(IO_3)_{3(s)} \rightleftharpoons Y^{3+} + 3IO_3^- \quad K_{sp} = 1.12 \times 10^{-10}$$

$$x \qquad 3x$$

$$K_{sp} = [Y^{3+}][IO_3^-]^3$$

$$1.12 \times 10^{-10} = (x)(3x)^3$$

$$1.12 \times 10^{-10} = 27x^4$$

$$x = \sqrt[4]{\frac{1.12 \times 10^{-10}}{27}}$$

$$x = 0.001427$$

$$= 1.43 \times 10^{-3}\ M$$

b) $[Y(NO_3)_3] = 0.45\,m$

$\therefore [Y^{3+}] = 0.45\,m$

$$Y(IO_3)_3 \rightleftharpoons Y^{3+} + 3IO_3^-$$

	Y^{3+}	$3IO_3^-$
	.45	—
	+ x	+ 3x
	.45 + x	+ 3x

$$K_{sp} = [Y^{3+}][IO_3^-]^3$$

$$1.12 \times 10^{-10} = (.45 + x)(3x)^3$$

$$x \ll .45$$

$$1.12 \times 10^{-10} = (.45)(27x^3)$$

$$1.12 \times 10^{-10} = 12.15x^3$$

$$x = \sqrt[3]{\frac{1.12 \times 10^{-10}}{12.15}}$$

$$= 0.000209$$

$$= 2.09 \times 10^{-4}\ m$$

$\therefore$ solubility ↓'s in presence of common ion

17. $HCOOH + H_2O \rightleftharpoons HCOO^- + H_3O^+$ $K_a = 1.8 \times 10^{-4}$

.25M, 300mL | .40M, 250mL | $V_T = 550\ mL$

determine new [ ] w new volume

$C_1V_1 = C_2V_2$

$(.25)(300) = (C_2)(550)$

$C_2 = 0.136\ M$

$C_1V_1 = C_2V_2$

$(.4)(250) = C_2(550)$

$C_2 = 0.1818\ M$

0.136	.1818	—
$-x$	$+x$	$+x$
$.136 - x$	$.1818 + x$	$+x$

$$K_a = \frac{[HCOO^-][H_3O^+]}{[HCOOH]}$$

$$1.8 \times 10^{-4} = \frac{(.1818 + x)(x)}{(.136 - x)}$$

$x \ll .1818$

$$1.84 \times 10^{-4} = \frac{(.1818)(x)}{.136}$$

$$x = \frac{(1.84 \times 10^{-4})(.136)}{(.1818)}$$

$$= 0.0001376$$

$\therefore [H_3O^+] = x$

$= .0001376\ M$

$pH = -\log(.0001376)$

$= 3.86$

18. $Al + NO^- \rightarrow NH_3 + Al^{3+}$ (Basic)

$Al \rightarrow Al^{3+} + 3e^-$ (×4)

$5OH^- + 5H^+ + NO^- \rightarrow NH_3 + \cancel{H_2O} + 5OH^-$

$\cancel{5H_2O}$

$4e^- + 5H_2O + NO^- \rightarrow NH_3 + 5OH^-$ (×3)

$\therefore$

$4Al \rightarrow 4Al^{3+} + \cancel{12e^-}$

$\cancel{12e^-} + 12H_2O + 3NO^- \rightarrow 3NH_3 + 15OH^-$

$4Al + 12H_2O + 3NO^- \rightarrow 4Al^{3+} + 3NH_3 + 15OH^-$

18 b

$AsH_3 + Zn^{2+} \rightarrow H_3AsO_4 + Zn$ (Acidic)

$4H_2O + AsH_3 \longrightarrow H_3AsO_4 + 8H^+ + 8e^-$

$Zn^{2+} + 2e^- \longrightarrow Zn$ (x4)

$4H_2O + AsH_3 \longrightarrow H_3AsO_4 + 8H^+ + \cancel{8e^-}$

$4Zn^{2+} + \cancel{8e^-} \longrightarrow 4Zn$

$4H_2O + AsH_3 + 4Zn^{2+} \rightarrow H_3AsO_4 + 8H^+ + 4Zn$

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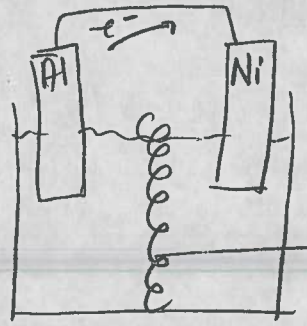
$Ni^{2+} + Al \rightarrow Ni + Al^{3+}$

$+2 \quad \emptyset \quad \emptyset \quad +3$

$Ni^{+2} + 2e^- \rightarrow Ni_{(s)}$ ger ∴ red. (cathode)

$Al \rightarrow Al^{3+} + 3e^-$ oxid LEO (anode)



anode (−) cathode (+) porous barrier

d) $E^\circ_{cell} = E^\circ_{cat} - E^\circ_{anode}$

$= -0.26 - (-1.66)$

$= +1.4\ V$

e) $Al \mid Al^{3+} \,||\, Ni \mid Ni^{2+}$

20 Ni - anode (+)

Al - cathode (−)

∴ $E^\circ = -1.4V$

- require battery to make rxn occur