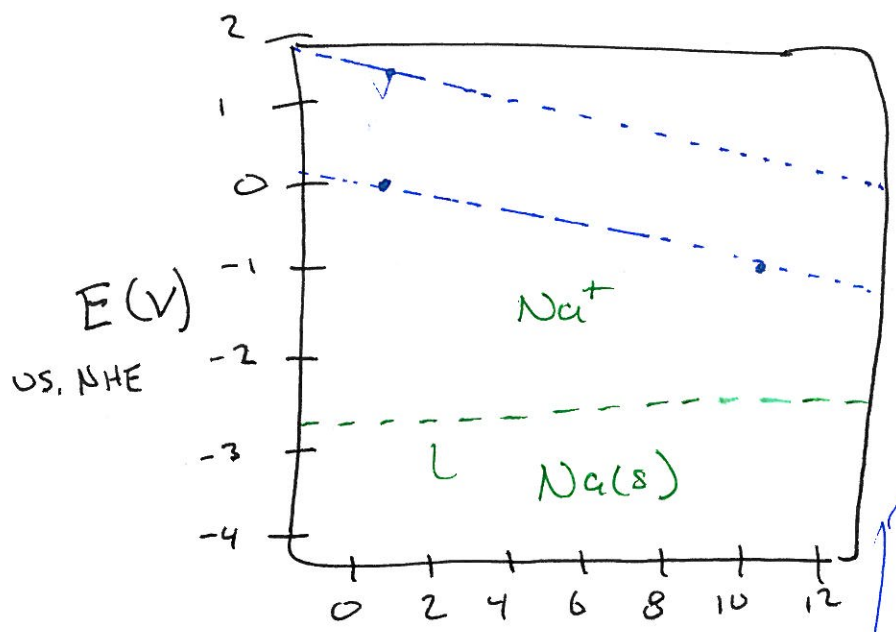
Lecture 4 - Potential - pH diagrams

- popularized by Marcel Pourbaix (1904 - 1998) (Russian) in 1938, Technical University of Delft.
- incredibly important for understanding corrosion

- applications in broad range of electrochemical, geochemical, ~~biochemical~~ biochemical, etc

→ Basic idea: a "phase" diagram that tells you under what conditions elements are stable in water, and under what conditions they "corrode" to form ions and what those ionic products will be.

Simple diagram - Na Diagram



(1) in any aqueous solution, two half reactions are always present:

$$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$$

water oxidation

$E = 1.23V - 0.059pH$

(derive this on next page)

$$2H^+ + 2e^- \rightarrow H_2$$

water reduction

$E = 0V - 0.059pH$

Q: where is the stability window for water?

Q: If you are outside of that window, how fast will water get oxidized or reduced?

Derivation of pH dependence:

$2H^+ + 2e^- \rightarrow H_2$ → basic thermo:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$$\Delta G = -nFE$$ (for a balanced cell reaction)

$$\Delta G = -nFE = -nFE^\circ + RT \ln Q$$

(* if we reference everything to the SHE at 0V then in principle the balanced equation would use the hydrogen electrode running in reverse. ...)

E is versus a reference... → $E = E^\circ + \frac{RT}{-nF} \ln Q$

$$Q = \frac{P_{H_2}}{[H^+]^2}$$, at 1atm $P_{H_2} \sim 1$

$$E = E^\circ + \frac{RT}{-nF} \ln [H^+]^{-2}$$

$n = 2$ (2e⁻ in reaction)

so, $E = E^\circ + \frac{-2}{-2} \frac{RT}{F} 2.3 \log [H^+]$

$$E = E^\circ - \frac{2.3RT}{F} pH$$

at 298K: $2.3RT/F = \boxed{0.059\,V}$

in electrochemistry, 60mV/decade is common observation

now consider putting Na(s) into the water, what would happen?

$$Na^+(aq) + e^- \rightarrow Na(s) \qquad E^\circ = -2.71\,V$$

what does this half reaction tell you?

→ remember also, this is at standard state

→ 1 M Na^+

→ how would this change if you had 10 mM Na^+?

Note: there is no dependence of $E_{Na^+/Na}$

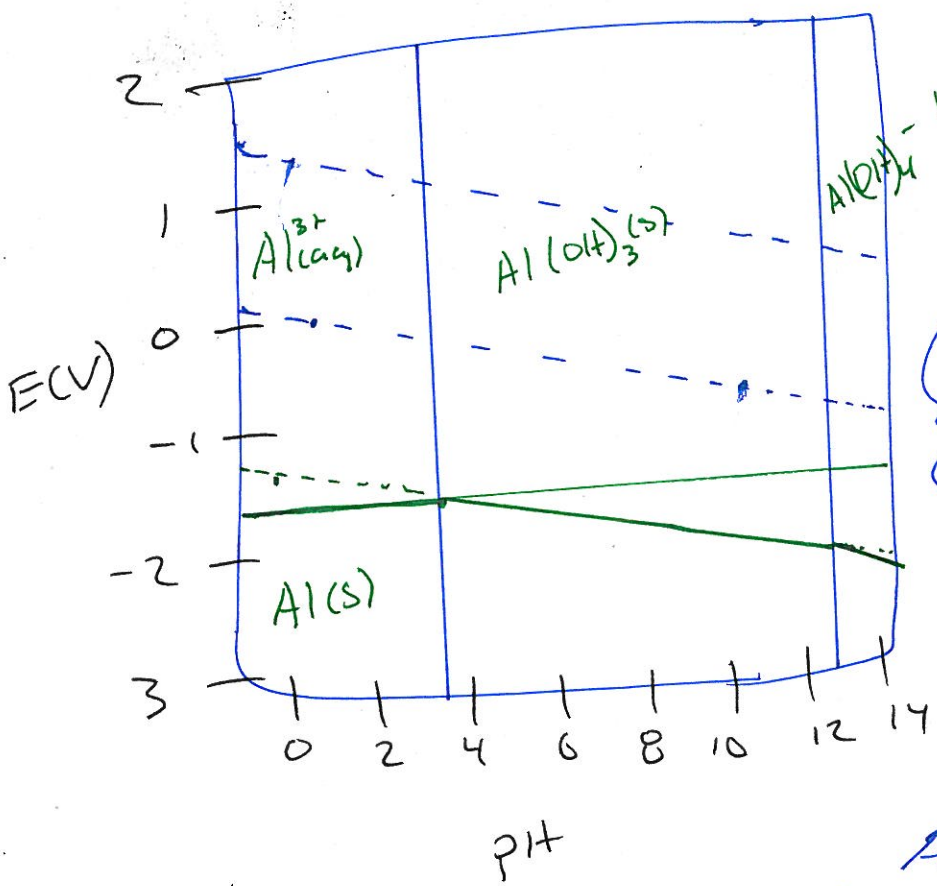
(cf $Na^+(aq) + e^- \rightarrow Na(s)$)

on pH — why?

no protons H^+ or hydroxide OH^- involved in equilibria!

Pourbaix diagrams are much more interesting when there are acid/base equilibria involved:

Consider Al: assume standard conditions (1M for all species)



what species do we know are there?

$2H^+ + 2e^- \rightarrow H_2$

$O_2 + 4e^- + 4H^+ \rightarrow H_2O$

↓

define window for water stability

What else?

$Al^{3+}_{(aq)} + 3e^- \rightarrow Al(s)$

$E^o = -1.68V$

again, no pH dependence?

Note: draw base diagram then go through one at a time the addition of all the lines.

Any other species?

Does Al exist as Al^{3+} in aqueous solution?

Other species include

$Al(OH)_3(s)$

$Al(OH_4)^-(aq)$

→ these are the predominant species at higher pH...

Also Al_{13} clusters exist "somewhere" on this pourbaix diagram...

So how do we know?

$$Al(OH)_3 + 3H^+ \rightarrow Al^{+3} + 3H_2O \quad K = 10^{10.2}$$

note this is written as a protonation constant.

We can solve for the pH where we have 1.0 M of $Al(OH)_3$ in Equilibrium w/ 1 M of Al^{+3}

$$K = \frac{[Al^{3+}]}{[Al(OH)_3][H^+]^3} = 10^{10.2}$$

$$[H^+] = \left(10^{-10.2}\right)^{1/3} = 10^{-10.2/3} = 10^{-3.4}$$

or $\boxed{pH = 3.4}$

→ we can draw this equillibria on an pourbaix diagram

Similiarly

$$Al(OH)_4^- + H^+ \rightarrow Al(OH)_3 + H_2O$$

$$K = 10^{12.4}$$

→ trivial to find that

for $[Al(OH)_4^-] = [Al(OH)_3] = 1\ M$

$$\boxed{pH = 12.4}$$

(so show this line also – this is just simple acid-base chemistry)

Q. Why is there no dependence on potential?

A. We are only considering Al in the +3 oxidation state!

So far we have only accounted for

$$Al^{+3} + 3e^- \rightarrow Al(s)$$

what about direct reduction of the hydroxides to Al(s)?

We write expressions for these as follows:

$$\boxed{3e^- + Al(OH)_3 + 3H^+ \rightarrow Al + 3H_2O \quad E^\circ = -1.47V \text{ vs NHE}}$$

So how do we add this line to the Pourbaix diagram? What is the slope? Is it flat?

$$E = E^\circ + \frac{-RT}{nF} \ln \frac{1}{[Al(OH)_3][H^+]^3}$$

$$n = 3, \quad [Al(OH)_3] = 1\ M$$

$$E = E^\circ + \frac{-RT}{3F} \ln \frac{1}{[H^+]^{+3}}$$

$$= E^\circ + \frac{RT}{F} \cdot 2.3 \log [H^+]$$

$$\boxed{= -1.47V + .06V \cdot pH}$$

↳ note again 60 mV/pH dependence...

↳ also note that Al(s) is easier to oxidize in neutral pH than in acid!

Remember: Electrons, solvents, and solids do not show up in the equilibrium expression!

if class is confused can write out the entire balanced equation w.r.t. H^+/H_2 at std. state.

Do we expect all equilibria w/ acid/base + O/R to give 60 mV/pH?

Now we consider the final reaction of interest:

$$3e^- + Al(OH)_4^- + 4H^+ \rightarrow Al + 4H_2O \quad E^\circ = -1.23V$$

Guess → what will the slope of this line?

$$E = E^\circ - \frac{RT}{nF} \ln \frac{1}{[Al(OH)_4^-][H^+]^4}$$

$$E = E^\circ - (.06V) \cdot \frac{4}{3} \cdot pH$$

(Question about soluble species content vs. total Al content...)

<u>80mV!</u>

→ add to graph...

So what can we tell from this graph?

Under what conditions is Al stable in water?

What happens at the surface?

→

What else can you tell?

is an electrode stable as an anode? what about as a cathode?

The general steps to construct an E-pH diagram

(1) Identify all species (Element + O + H ect).

(2) Start lower left corner of E-pH framework,

a. arrange species in vertical order, ↑ ox up.

b. arrange same oxidation number horizontal w/ decreasing protonation (increasing hydroxylation)

(3) draw approximate lines between species

(4) write out equations for all the transformations.

- half reactions (change in oxidation state) ~~write~~ written as reductions
- acid base reactions written only in terms of H^+/H_2O (no OH^-)

(5) find ΔG° for all species → $\Delta G^\circ_{rxn} = \sum \Delta G^\circ_{f,products} - \sum \Delta G^\circ_{f,reactants}$

(6) use ΔG° to find E°, K for redox / acid base reactions

$$\Delta G^\circ = -nFE^\circ, \quad \Delta G^\circ = RT \ln K$$

(7) a. use Nernst Equation to write out expressions for all redox transitions as function of pH and [species]

b. for acid-base reactions write out expression for pH as function of concentration of species. (in book they set "center" species to a concentration of 1) but $Ga(OH)_3$ is a solid...

(8) Draw lines, erase portions when overlaps occur.

Online example

www.doitpoms.ac.uk

→ learning packages

construction of a

→ pourbaix diagram

→ go through an Example.

Reactions and applications

E-pH diagrams involve two types of reactions
(1) non-redox full reactions (acid/base)
(2) redox half-reactions

→ to write full redox reaction need two half reactions

→ consider cross-section cut into E-pH diagram

→ show diagram on computer screen

eg. Zn:

$$Zn^{2+} + 2e^- \Rightarrow Zn(s) \quad E^\circ = -0.763\,V$$

- in order to drive this reaction there must be a species in solution able to ~~accept~~ take these electrons w/ reduction potential more negative than $E_{Zn^{2+}/Zn}$
- if you add Zn^{2+} to water do you expect to form any Zn (s)?
- Now, imaging you add Zn (s) to an aqueous solution. – looking at the Pourbaix diagram, what reactions might you expect to drive?

$$2H^+ + 2e^- \rightarrow H_2$$

$$O_2 + 4H^+ + 4e^- \rightarrow H_2O$$ (dissolved oxygen must be present)

Based on thermodynamics, which one will you drive? Based on kinetics / mass transport?

→ Overlay 2 pourbaix diagrams – predict reactions between elements