Acids, bases and solution equilibria

A four lecture course for the 1st year

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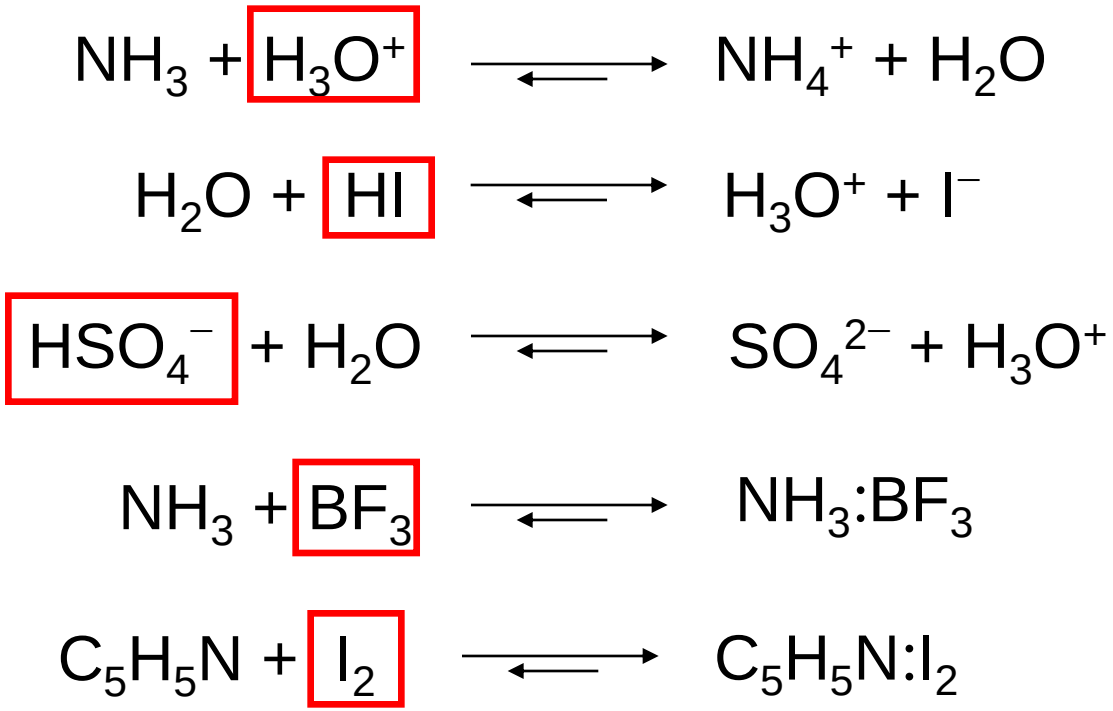
http://course.chem.ox.ac.uk/acids-bases-and-solutions-equilibria-year-1-2014.aspx

http://goicoechea.chem.ox.ac.uk/teaching.html

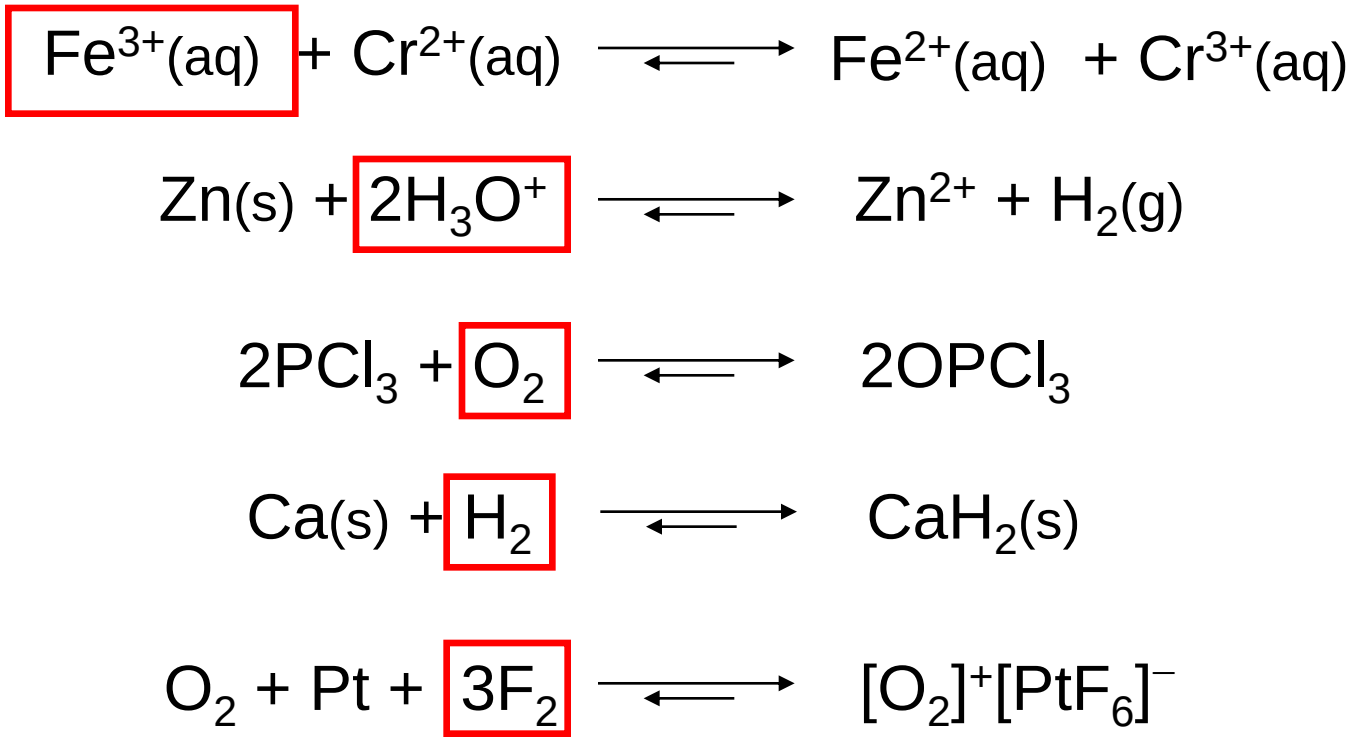
Acid-base reactions



Species highlighted act as acids

Redox reactions

A redox reaction is a reaction in which there is a change in oxidation state



One or two electrons are transferred entirely

Species highlighted act as oxidants

Definitions of Acid/Base

Arrhenius/Ostwald

Brønsted/Lowry

Lux/Flood

‘Solvent system’

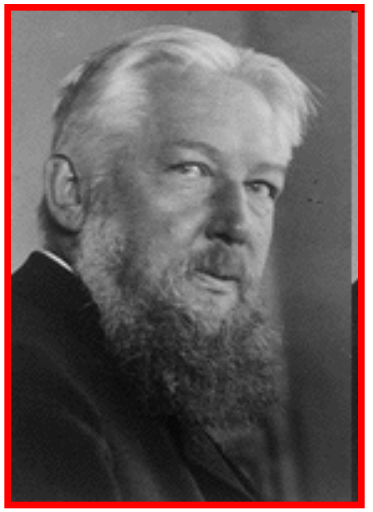
Lewis

Usanovich

Arrhenius/Ostwald

Acids and bases dissociate in H_2O, releasing H^+ (H_3O^+) and OH^-.

Arrhenius



Ostwald

$$H_2O \rightleftharpoons H^+(aq) + OH^-(aq)$$

$H^+(aq)$ is an acid

$OH^-(aq)$ is a base

Brønsted/Lowry

Proton theory retained but the definition is now independent of solvent

Brønsted

Lowry

An acid is a proton donor and a base is a proton acceptor.

$NH_4^+ + NH_2^- \rightleftharpoons 2NH_3$

Other solvents are also capable of self-ionisation

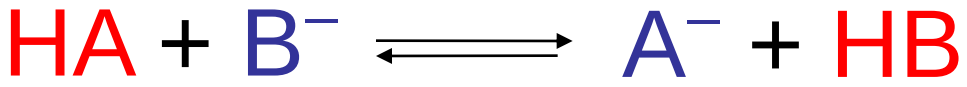
$HCl + NH_3 \rightleftharpoons [NH_4]^+Cl^-$

Donor acid *Acceptor base*

Proton transferred from acid to base

Brønsted/Lowry

Every acid has a conjugate base and every base has a conjugate acid



The conjugate base of a weak acid is a strong base, and the conjugate base of a strong acid is a weak base.

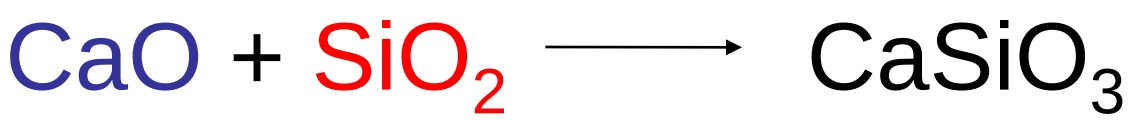
TRUE FACT!

Lux/Flood

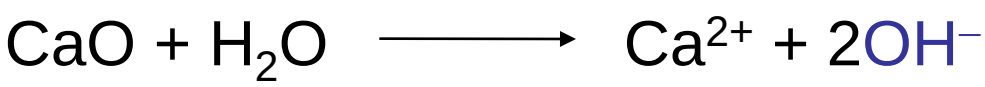
A definition for anhydrous/dry systems: used in solid state chemistry

The concept focuses on the oxide ion (O^{2-})

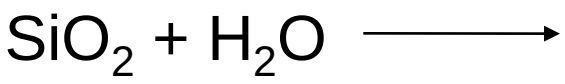
A base is a oxide donor and an acid is an oxide acceptor.



The Lux-Flood base is a basic anhydride



The Lux-Flood acid is an acid anhydride.



Solvent system

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$$

$$2H_2SO_4 \rightleftharpoons H_3SO_4^+ + HSO_4^-$$

cation^{solv} *anion*^{solv}

This definition is based on solvent autoionisation

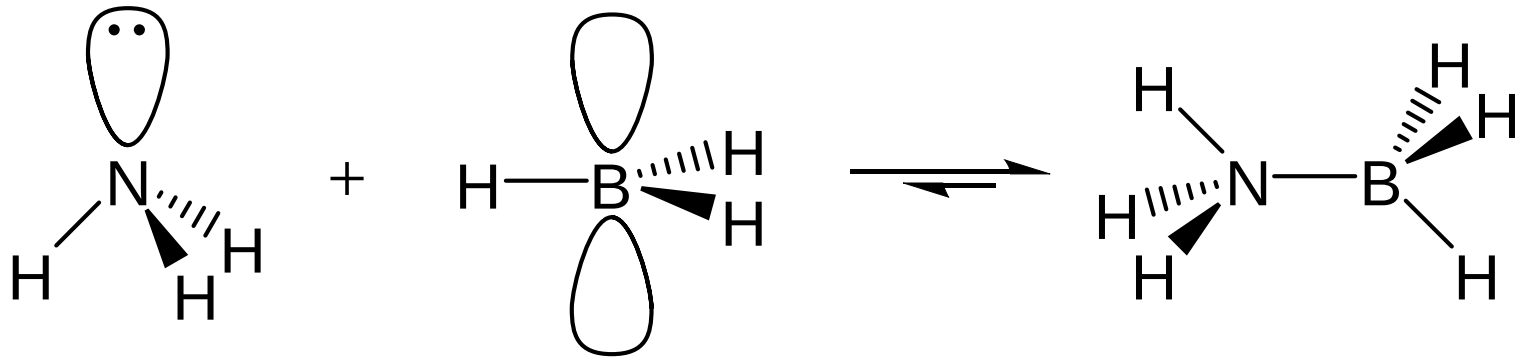
An acid is a species that increases the concentration of *cation*^{solv}

A base is a species that increases the concentration of *anion*^{solv}

Lewis

An acid is an electron pair acceptor
A base is a an electron pair donor

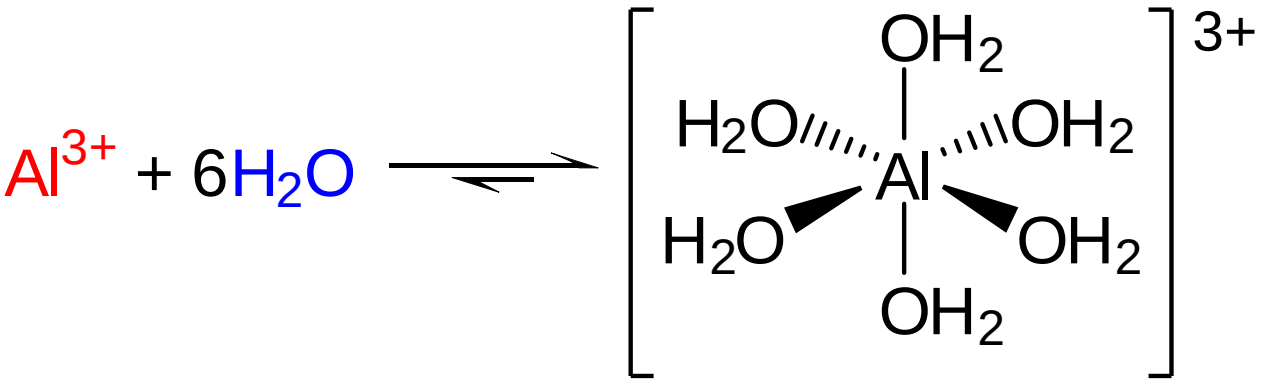
$$NH_3 + BF_3 \rightleftharpoons NH_3BF_3$$



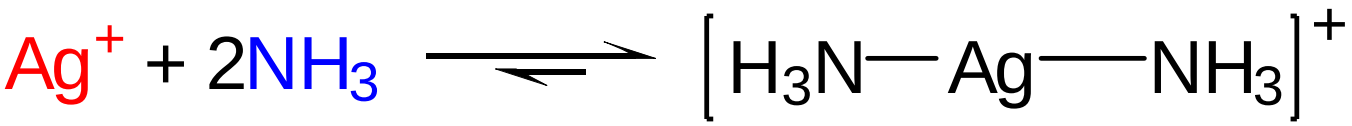
Has ‘lone’ pair

Has six valence electrons

More examples of Lewis acid/base interactions



All metal cations in donor solvents are Lewis acids interacting with solvent molecules which act as Lewis bases

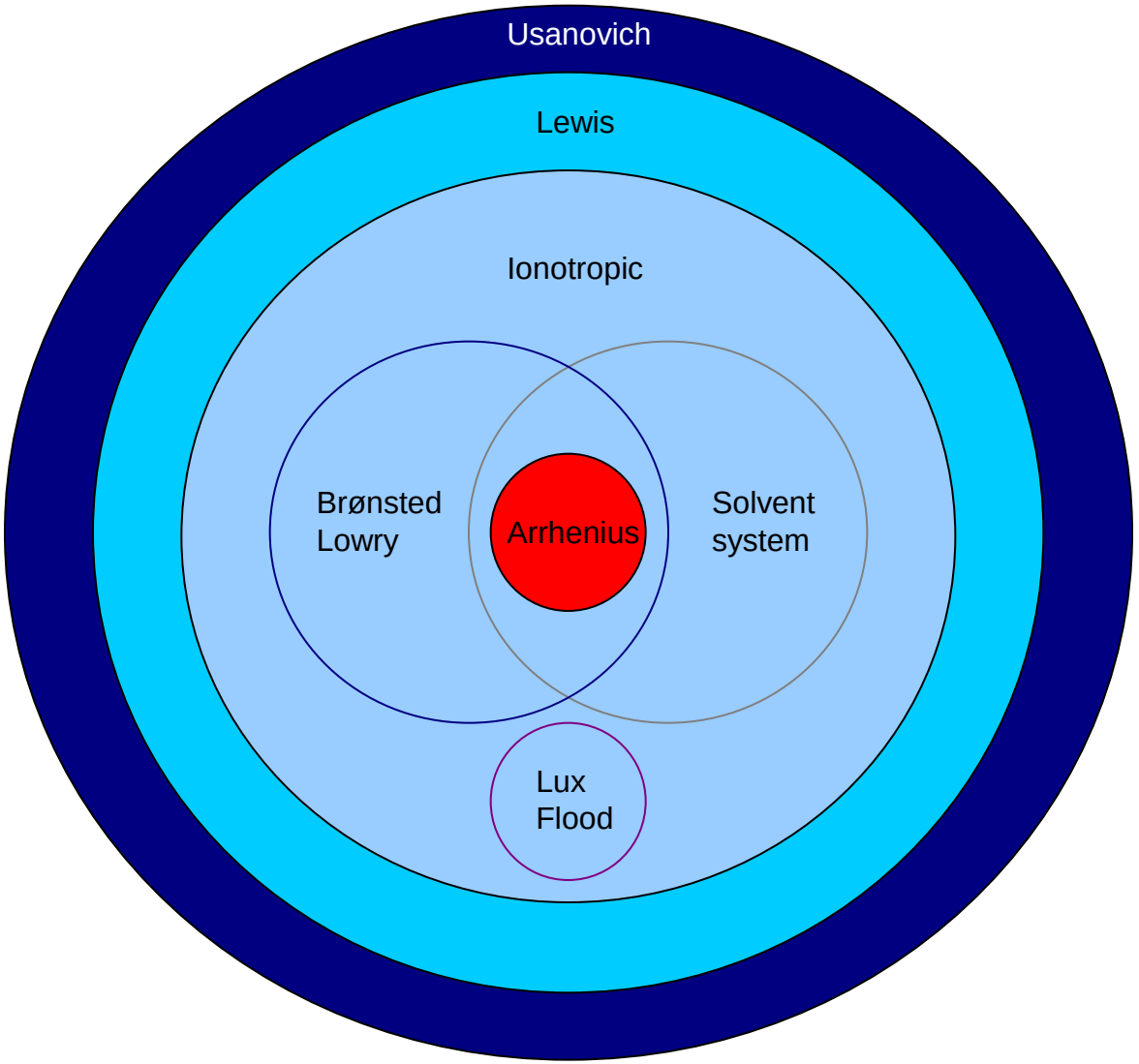


Usanovich

A broad definition which encompasses all other acid/base concepts

An acid is a species that reacts with bases. It gives up cations or accepts anions or electrons

A base is a species that reacts with acids. It gives up anions, combines with cations, or donates electrons.



Proton equilibria in water

$$HX_{(aq)} + H_2O \rightleftharpoons H_3O^+ + X^-_{(aq)}$$

$$K_a = \frac{[H_3O^+][X^-]}{[HX]}$$

$$pK_a = -\log_{10} K_a$$

$$pH = -\log_{10}[H_3O^+]$$

Autoprotolysis

$$2H_2O \rightleftharpoons H_3O^+_{(aq.)} + OH^-_{(aq.)}$$

$$K_w = [H_3O^+][OH^-]$$

For H_2O, $K_w = 10^{-14}$ at 25° C

Easy way to treat pK_a

$$\textit{Since} \quad K_a = \frac{[H_3O^+][X^-]}{[HX]}$$

$K_a = [H^+_{(aq.)}]$ when $[HX] = [X^-]$ *i.e.* when HX is 50% converted to X^-

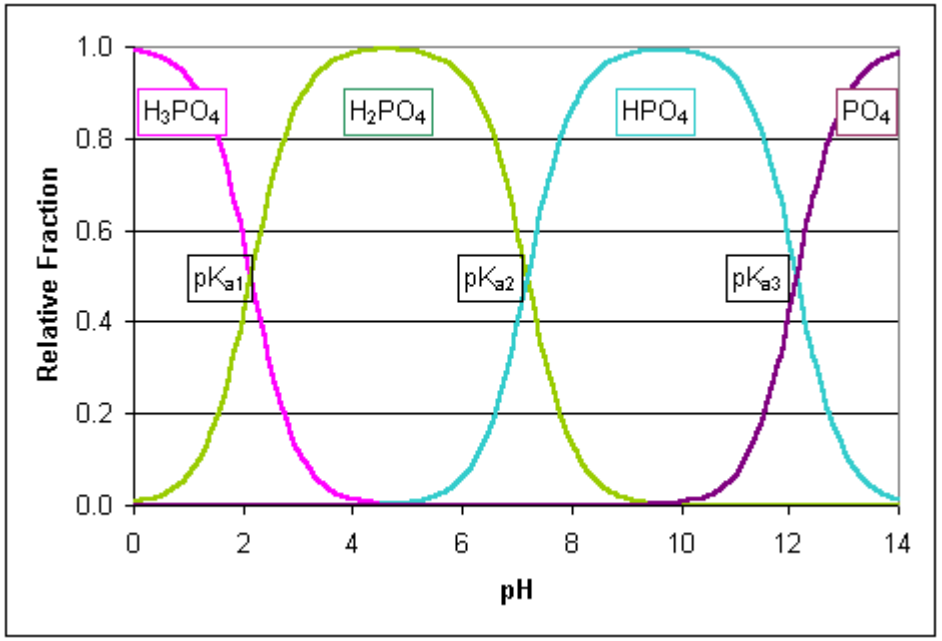
pK_a is pH at which HX is 50% dissociated

Acid	HA	A^-	K_a	pK_a
Hydriodic	HI	I^-	10^{11}	–11
Perchloric	$HClO_4$	ClO_4^-	10^{10}	–10
Hydrobromic	HBr	Br^-	10^9	–9
Hydrochloric	HCl	Cl^-	10^7	–7
Sulfuric	H_2SO_4	HSO_4^-	10^2	–2
Nitric	HNO_3	NO_3^-	10^2	–2
Hydronium ion	H_3O^+	H_2O	1	0.0
Chloric	$HClO_3$	ClO_3^-	10^{-1}	1
Sulfurous	H_2SO_3	HSO_3^-	1.5×10^{-2}	1.81
Hydrogensulfate ion	HSO_4^-	SO_4^{2-}	1.2×10^{-2}	1.92
Phosphoric	H_3PO_4	$H_2PO_4^-$	7.5×10^{-3}	2.12
Hydrofluoric	HF	F^-	3.5×10^{-4}	3.45
Formic	HCOOH	HCO_2^-	1.8×10^{-4}	3.75
Ethanoic	CH_3COOH	$CH_3CO_2^-$	1.74×10^{-5}	4.76
Pyridinium ion	$HC_5H_5N^+$	C_5H_5N	5.6×10^{-6}	5.25
Carbonic	H_2CO_3	HCO_3^-	4.3×10^{-7}	6.37
Hydrogen sulfide	H_2S	HS^-	9.1×10^{-8}	7.04
Dihydrogenphosphate ion	$H_2PO_4^-$	HPO_4^{2-}	6.2×10^{-8}	7.21
Ammonium ion	NH_4^+	NH_3	5.6×10^{-10}	9.25
Hydrocyanic	HCN	CN^-	4.9×10^{-10}	9.31
Hydrogencarbonate ion	HCO_3^-	CO_3^{2-}	4.8×10^{-11}	10.32
Hydrogenphosphate ion	HPO_4^{2-}	PO_4^{3-}	2.2×10^{-13}	12.67
Hydrogensulfide ion	HS^-	S^{2-}	1.1×10^{-19}	19

Polyprotic acids

A polyprotic acid loses protons in succession, with each deprotonation becoming progressively less favourable.

The behaviour of such species in solution be represented by a distribution diagram



$pK_{a1} = 2.21$
$pK_{a2} = 7.21$
$pK_{a3} = 12.68$

$$\alpha(H_3PO_4) = \frac{[H_3PO_4]}{[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}]}$$

Hammet acidity function

$$H^+ + X^- \rightleftharpoons HX$$

For any base B:

$$H^+ + B \rightleftharpoons HB^+$$

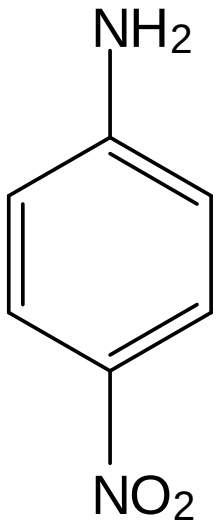
$$H_0 = pK_{BH^+} - \log \frac{[BH^+]}{[B]}$$

$\frac{[BH^+]}{[B]}$ can be measured with a dye

Very concentrated solutions: Hammet acidity function

$$HX + Ind \rightleftharpoons IndH^+ + X^-$$

Ind is a coloured indicator *e.g.*



4-Nitroaniline

$$H_0 = pK_{IndH^+} + \log \frac{[Ind]}{[IndH^+]}$$

H_0 is the Hammett function of HX

Pure H_2SO_4, $H_0 = -11.9$

Superacid (HSO_3F), $H_0 = -15.1$

Strength of Brønsted acids and bases

Two principal factors control acid/base strength:

1) Inherent properties of the species itself

To quantify this value we must measure proton transfer reactions in the gas phase.
Chemistry controlled by ΔH

$$H^+(g) + X(g) \longrightarrow HX^+(g) \qquad A_p = -\Delta H$$

A_p = proton affinity of X

2) Environment (e.g. solvation)

WORTH REMEMBERING!

Proton-Transfer reactions

$$HA_{(g)} + B_{(g)} \rightleftharpoons A^-_{(g)} + HB^+_{(g)}$$

Can be considered as two "half reactions"

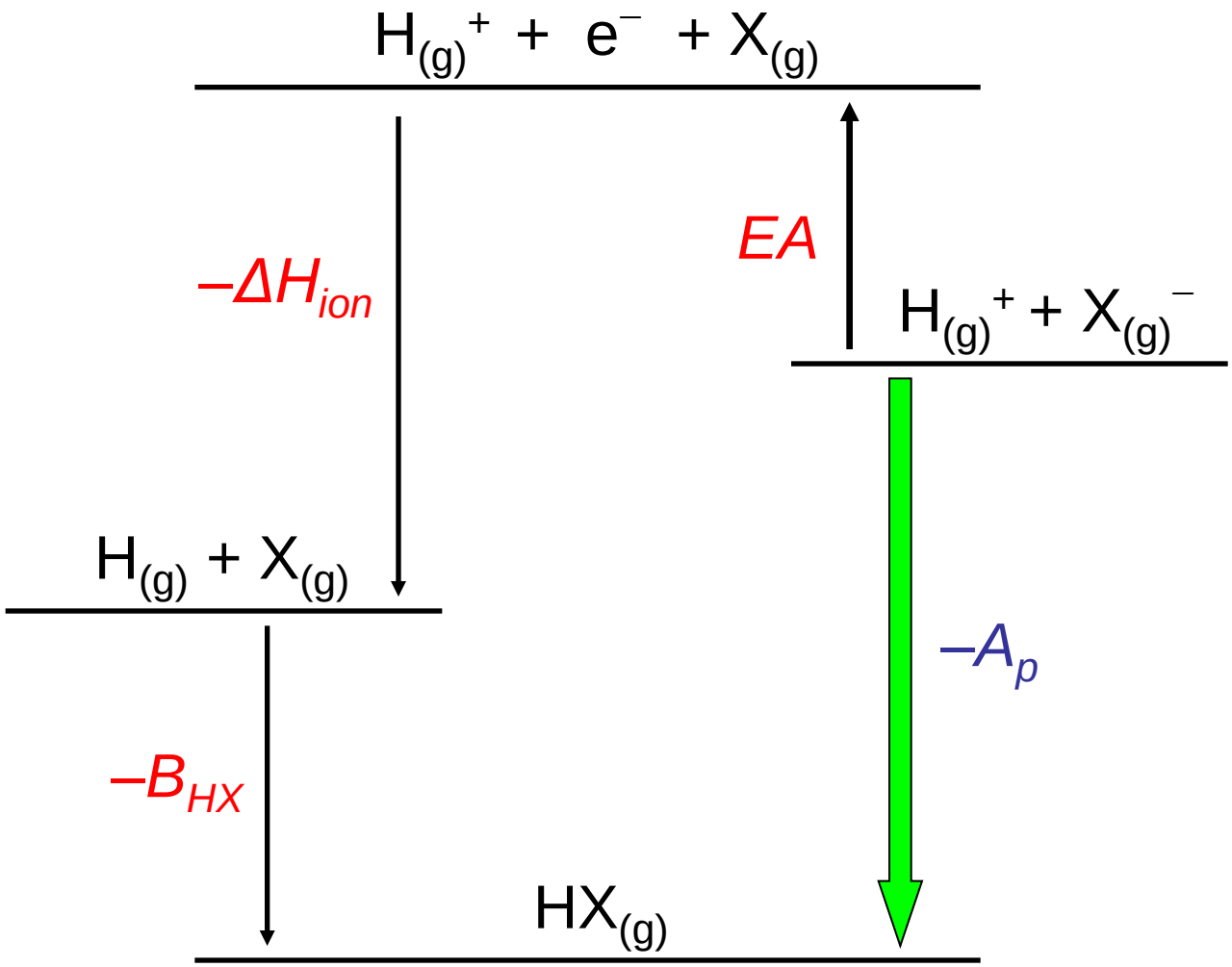
$$H^+_{(g)} + B_{(g)} \overset{\Delta H_B}{\rightleftharpoons} HB^+_{(g)}$$

$$H^+_{(g)} + A^-_{(g)} \overset{\Delta H_A}{\rightleftharpoons} HA_{(g)}$$

$$\text{Then } \Delta H_{rxn} = \Delta H_B - \Delta H_A$$

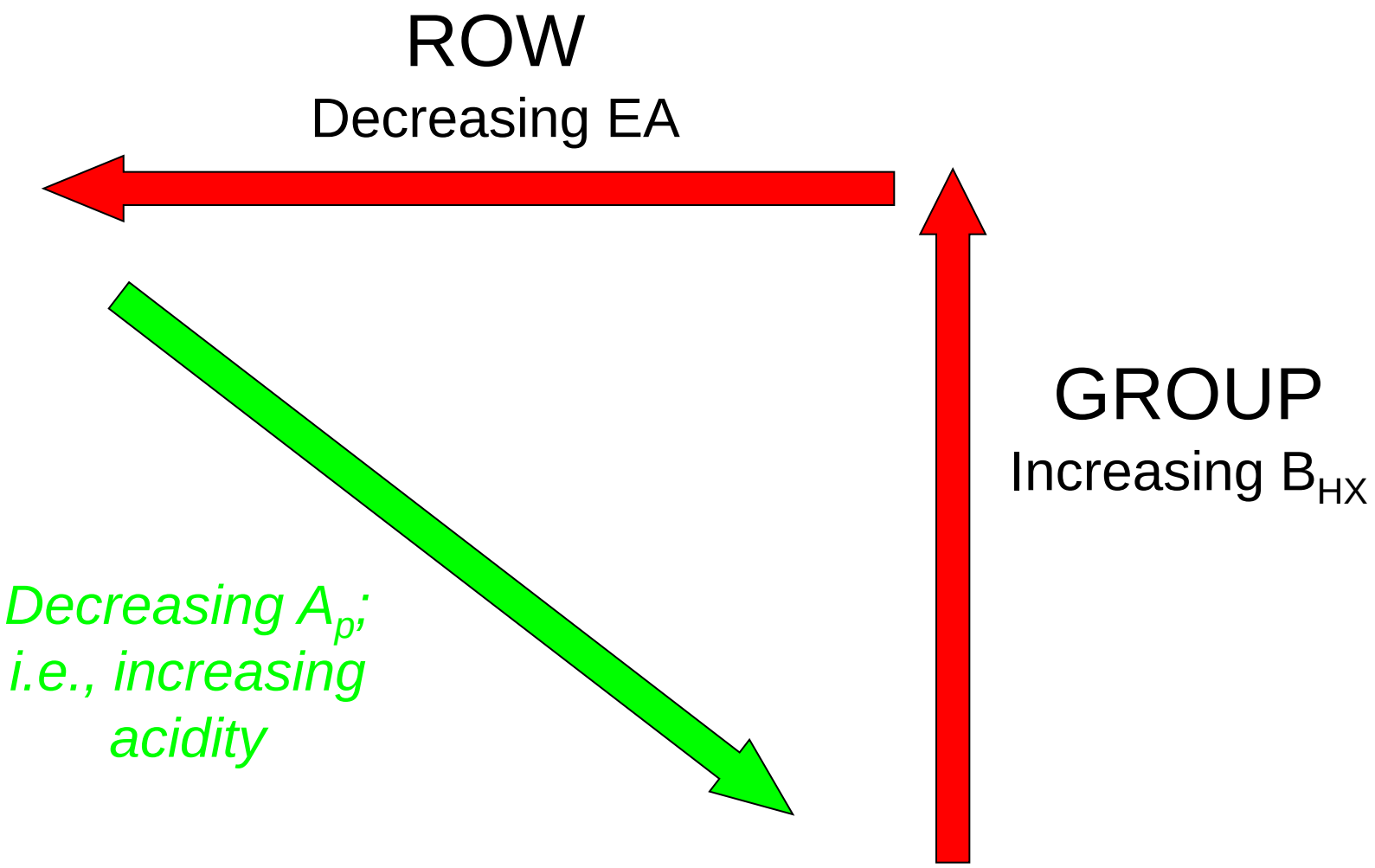
$$\Delta H_{rxn} = A_{p(A)} - A_{p(B)}$$

The reaction is favourable is $A_{p(B)} > A_{p(A)}$



$$A_p = B_{HX} + \Delta H_{ion} - EA$$

$$A_p = B_{HX} + \Delta H_{ion} - EA$$



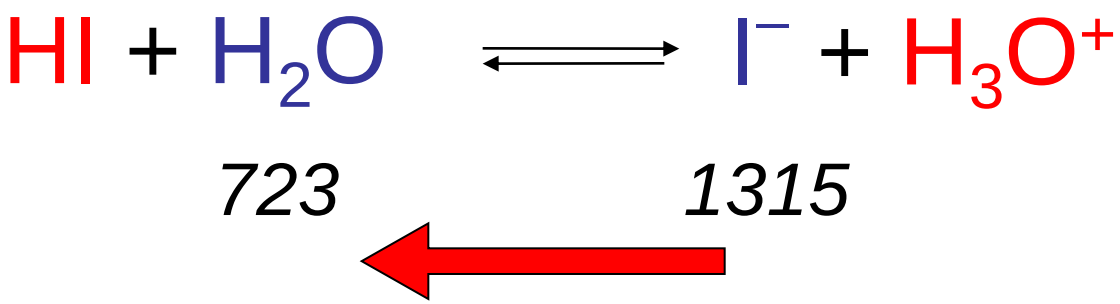
Proton affinity (A_p; KJ/mol)

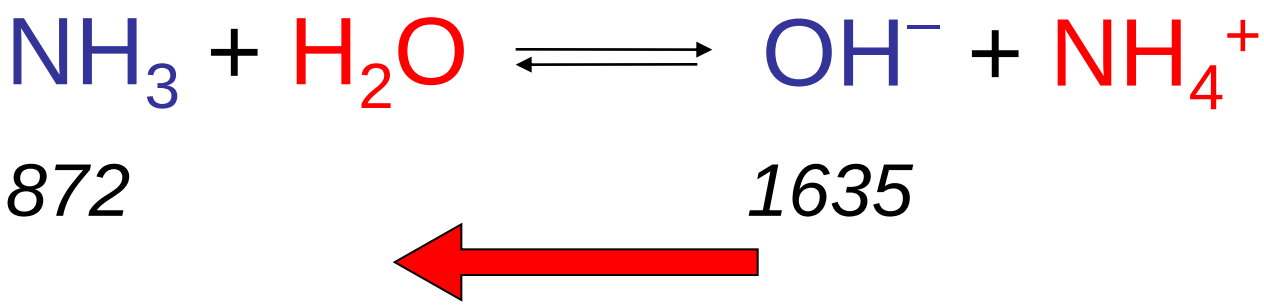
H^-	CH_3^-	NH_2^-	OH^-	F^-
1675	*1745*	*1689*	*1635*	*1554*
	SiH_3^-	PH_2^-	SH^-	Cl^-
	1554	*1552*	*1469*	*1395*
	GeH_3^-	AsH_2^-	SeH^-	Br^-
	1509	*1515*	*1466*	*1354*
				I^-
				1315

A_p for H_2O: 723

PH_2^- and F^- have almost identical A_p values but their pK_a values differ (27 to 3.45, respectively) making F^- a much stronger acid in water.

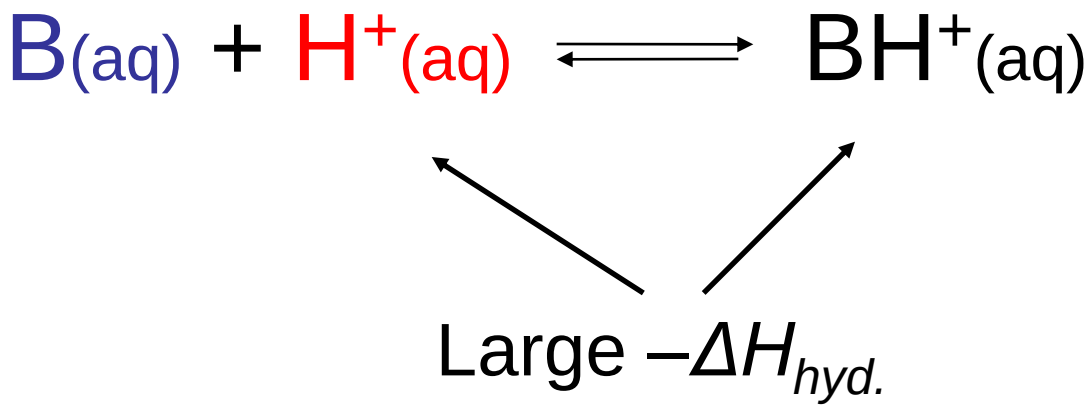
Predictions ignoring solvation



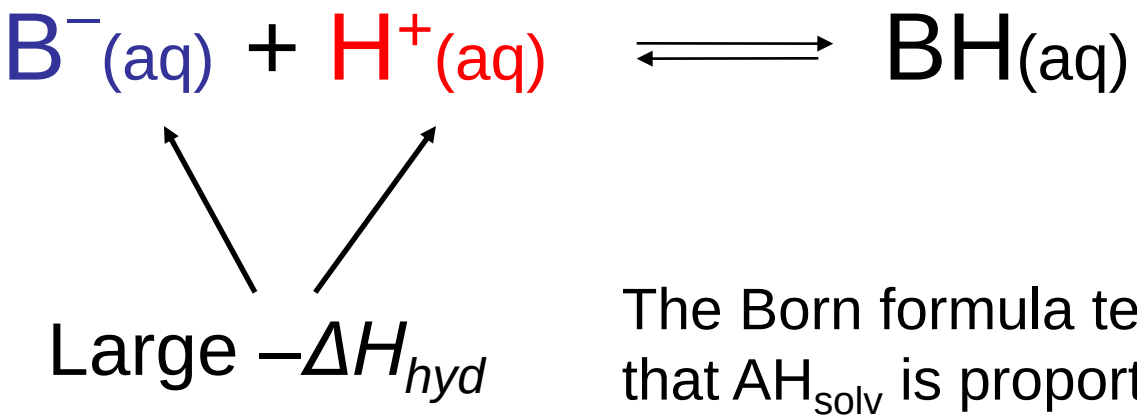


This can’t be right, other factors must be at play

Taking into account solvation effects



or alternatively…



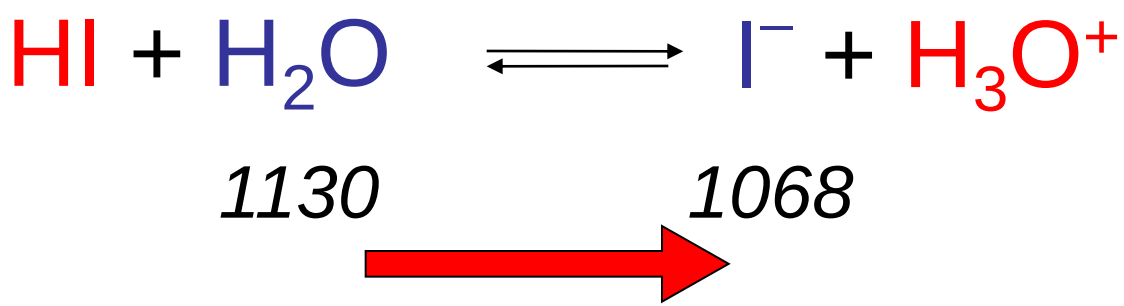
The Born formula tells us that AH_{solv} is proportional to: $\frac{-z^2}{r}$

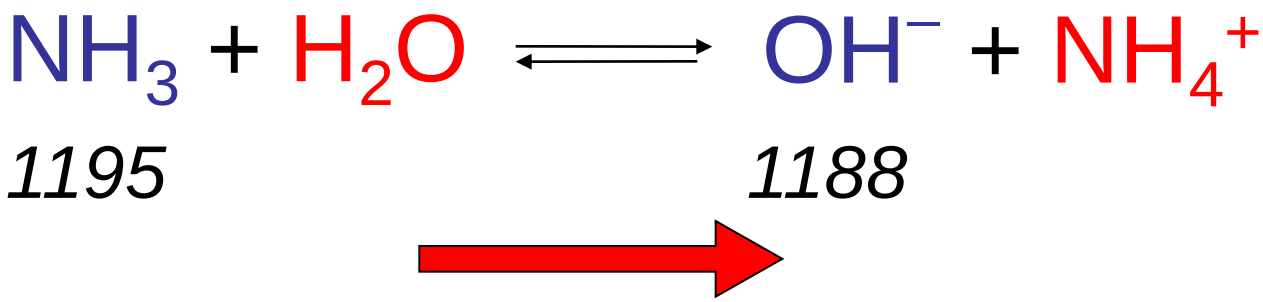
Effective proton affinity (A_p'; KJ/mol) and pK_a

H^-	CH_3^-	NH_2^-	OH^-	F^-
	1380	*1351*	*1188*	*1150*
	49	*39*	*15.7*	*3.2*
	SiH_3^-	PH_2^-	SH^-	Cl^-
	1283			*1090*
	35	*27*	*7.05*	*–6.1*
	GeH_3^-	AsH_2^-	SeH^-	Br^-
				1079
	25	*23*	*3.8*	*–8*
				I^-
				1068
				–9

A_p' for H_2O: 1130

Predictions taking into account solvation





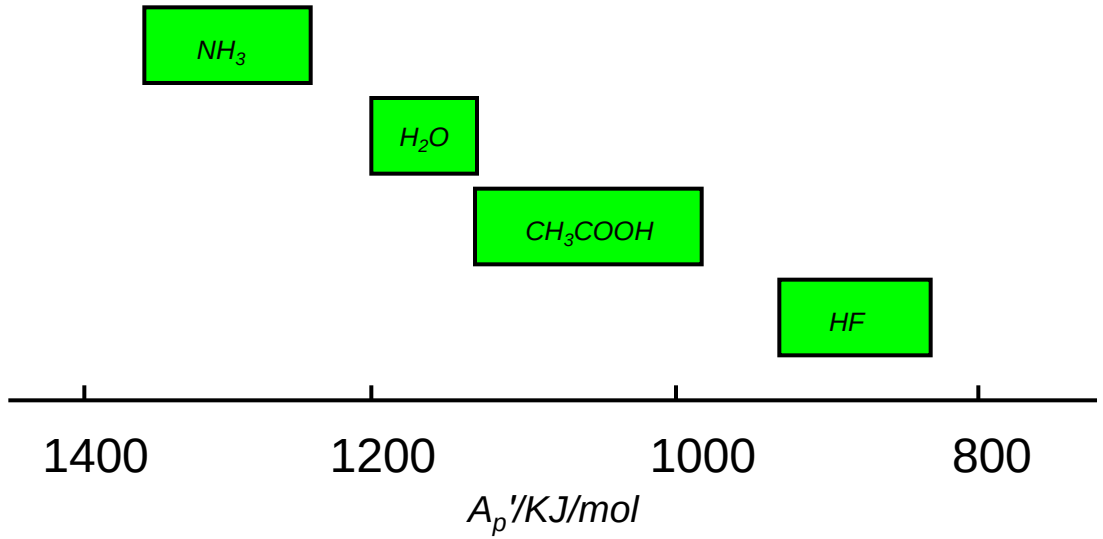
Range of discrimination

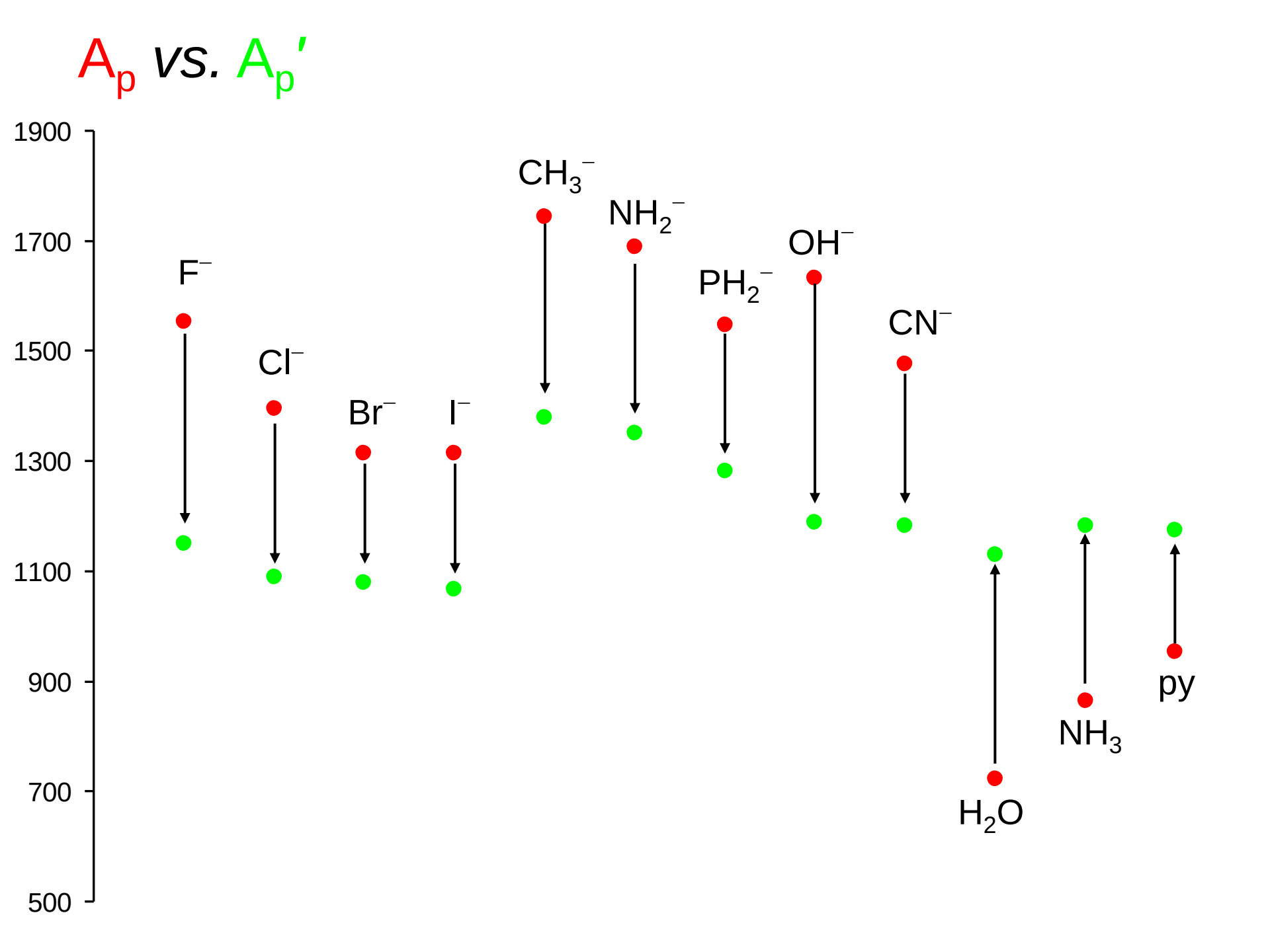
$$HY + HY \rightleftharpoons H_2Y^+ + Y^-$$

$$K_{auto} = [H_2Y^+][Y^-]$$

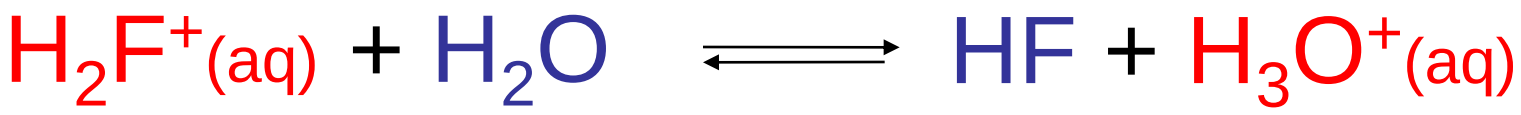
$$pK_{auto} = -\log K_{auto}$$

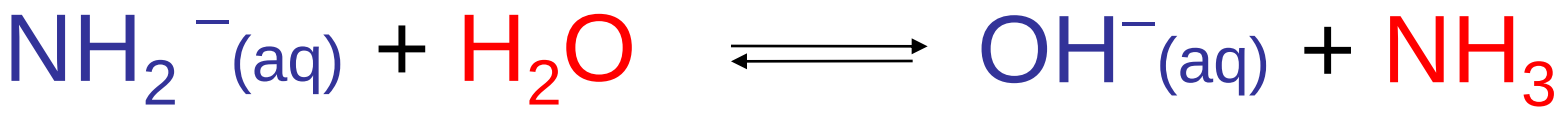
Acid-base discrimination windows




A_p *vs.* A_p'
1900
1700
1500
1300
1100
900
700
500
F^-
Cl^-
Br^-
I^-
CH_3^-
NH_2^-
PH_2^-
OH^-
CN^-
H_2O
NH_3
py

Solvent levelling

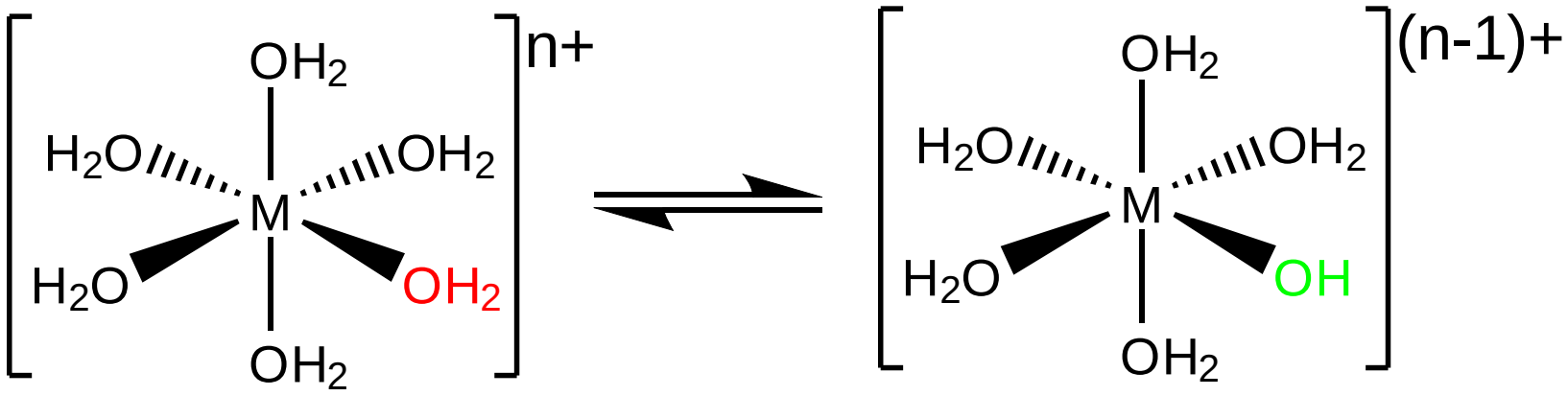




Strongest acid that can exist is H_2Y^+

Strongest base is Y^-

Metal aqua ion acidity



$$M_{aq.}^{n+} \rightleftharpoons MOH^{(n-1)+} + H_{aq.}^{+}$$

Arrange in order of increasing acidity:

$[Na(OH_2)_6]^+$, $[Sc(OH_2)_6]^{3+}$, $[Mn(OH_2)_6]^{2+}$, $[Ni(OH_2)_6]^{2+}$

$[Na(OH_2)_6]^+ < [Mn(OH_2)_6]^{2+} < [Ni(OH_2)_6]^{2+} < [Sc(OH_2)_6]^{3+}$

Hydrolysis constants (pK_{hyd}) for cations at 25° C

Li^+ *13.9*	Be^{2+} *6.2*											
Na^+ *14.7*	Mg^{2+} *11.4*											Al^{3+} *5.0*
K^+ *-*	Ca^{2+} *12.6*	Sc^{3+} *4.7*	Ti^{3+} *2.3*	V^{2+} *6.5*	Cr^{2+} *8.7*	Mn^{2+} *10.6*	Fe^{2+} *10.1*	Co^{2+} *9.6*	Ni^{2+} *10.0*	Cu^{2+} *7.6*	Zn^{2+} *9.5*	Ga^{3+} *2.6*
				V^{3+} *2.6*	Cr^{3+} *3.9*		Fe^{3+} *2.0*	Co^{3+} *3.2*				
Rb^+ *-*	Sr^{2+} *13.1*	Y^{3+} *8.0*						Rh^{3+} *3.2*	Pd^{2+} *1.6*	Ag^+ *11.8*	Cd^{2+} *7.9*	In^{3+} *3.2*
Cs^+ *-*	Ba^{2+} *13.3*	La^{3+} *9.5*						Ir^{3+} *4.8*	Pt^{2+} *>2.5*		Hg^{2+} *2.5*	Tl^+ *13.3*

Burgess, J. *Metal Ions in Solution*; Ellis Horwood: Chichester, 1978, pp. 264-265

Pauling's rules for oxoacids

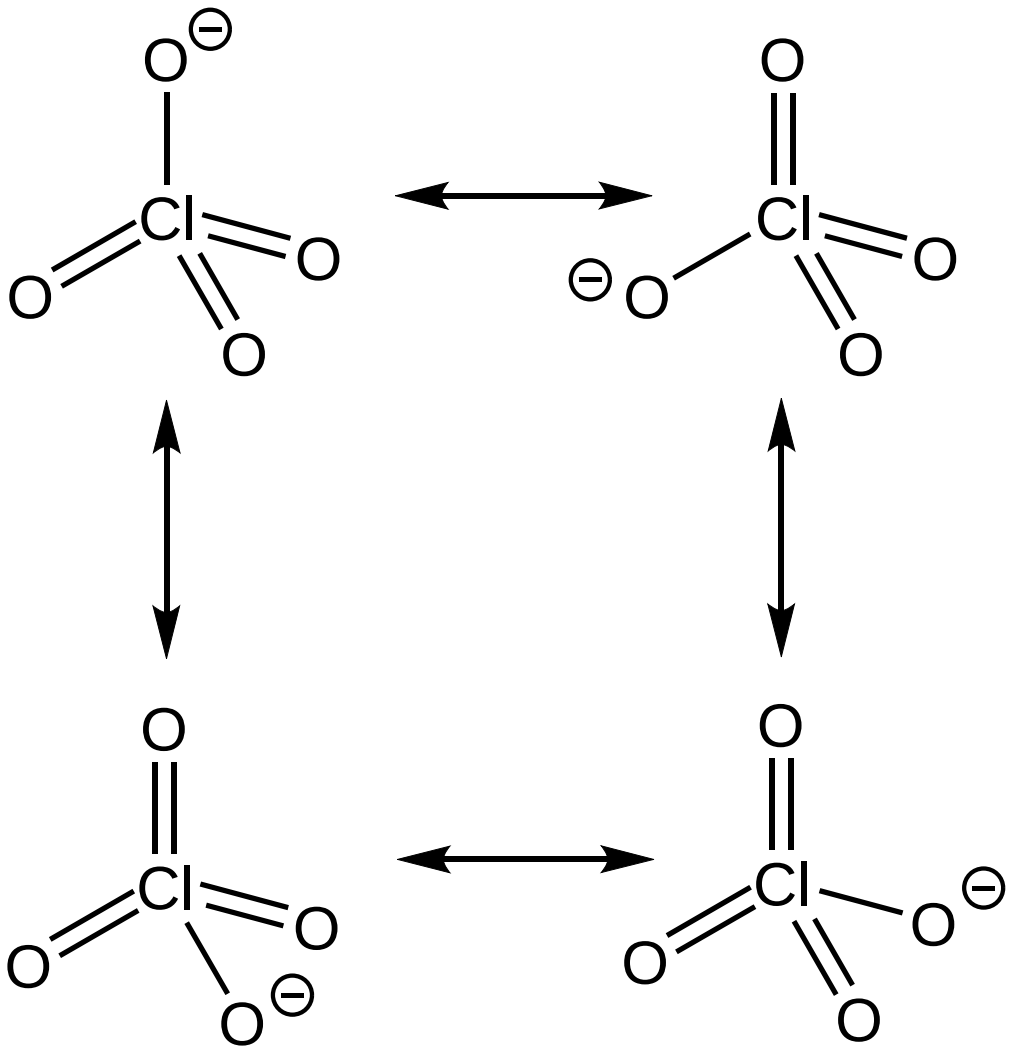
$O_pE(OH)_q$

Rule 1: $pK_{a1} = 8 - 5p$

WORTH REMEMBERING!

The higher the number of oxo- groups bound to the central element, the greater the acidity of the acid.

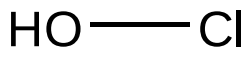
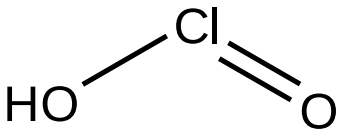
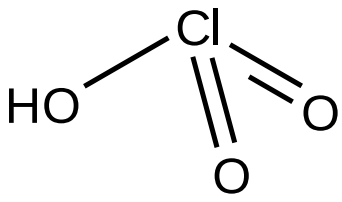
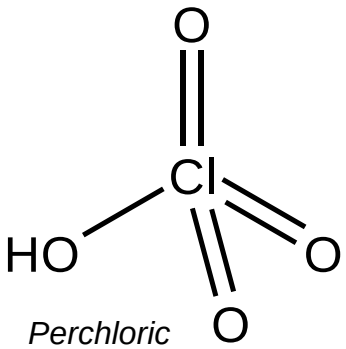
$HClO_4$; $O_3Cl(OH)$; $pK_a = -10$



The higher acidity is due to the greater number of resonance structures of the conjugate base

Pauling's rules to the test

$$pK_{a1} = 8 - 5p$$

p =	*0*	*1*	*2*	*3*
				
	Hypochlorous	*Chlorous*	*Chloric*	*Perchloric*
pK_a =	*7.2*	*2.0*	*-1.0*	*-10*

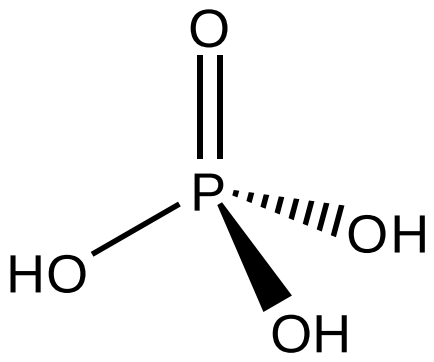
Pauling's rules for oxoacids

The successive pK_a values of polyprotic acids (those with q > 1), increase by five for each successive proton transfer

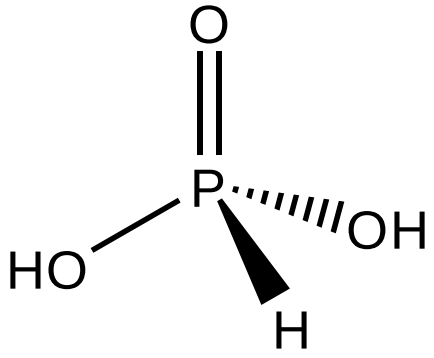
Rule 2:

$$pK_{a2} = pK_{a1} + 5$$
$$pK_{a3} = pK_{a2} + 5$$
$$pK_{a4} = pK_{a3} + 5$$

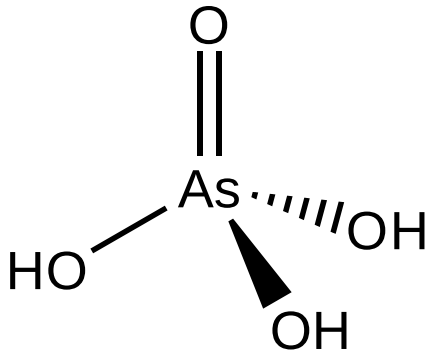
WORTH REMEMBERING!



$pK_{a1} = 2.1$
$pK_{a2} = 7.4$
$pK_{a3} = 12.7$



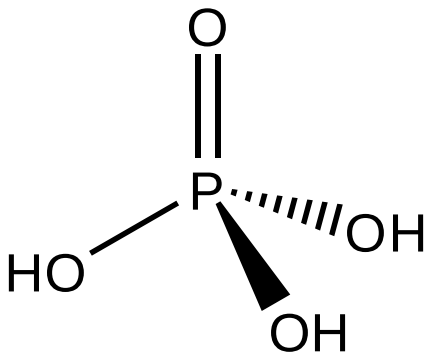
$pK_{a1} = 1.8$
$pK_{a2} = 6.6$



$pK_{a1} = 2.3$
$pK_{a2} = 6.9$
$pK_{a3} = 11.5$

Compare the acidities of the following acids:

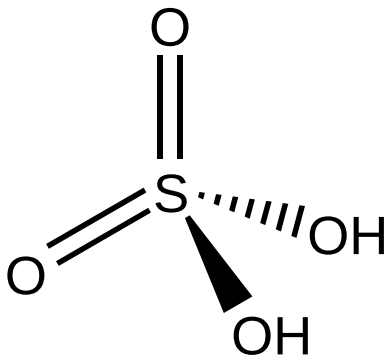
H_3PO_4



$pK_a = 8 – 5p = 3$

Real value: 2.12

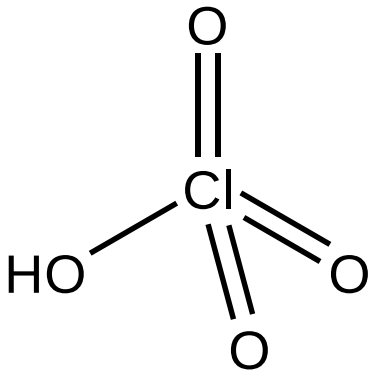
H_2SO_4



$pK_a = 8 – 5p = –2$

Real value: –2

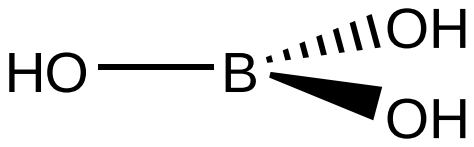
$HClO_4$



$pK_a = 8 – 5p = –7$

Real value: –10

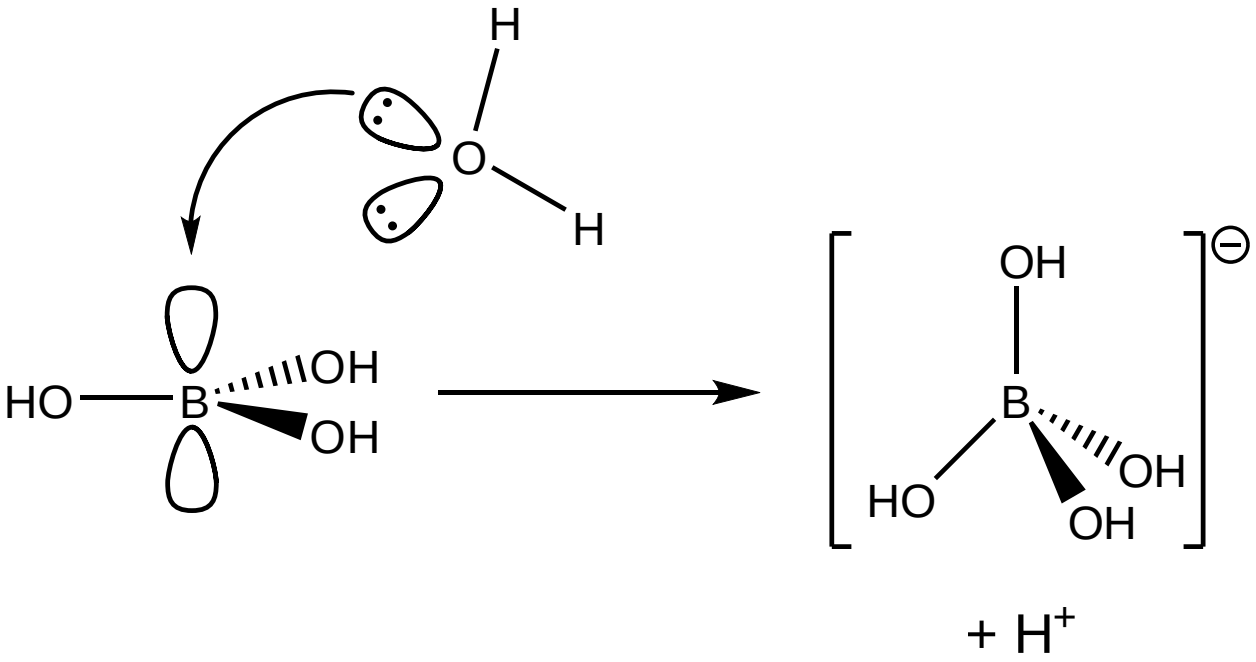
So what's up with boric acid?



According to Pauling's first rule for oxo-acids it should have a pK_a of 8.
Tabulated values indicate $pK_a = 9.2$

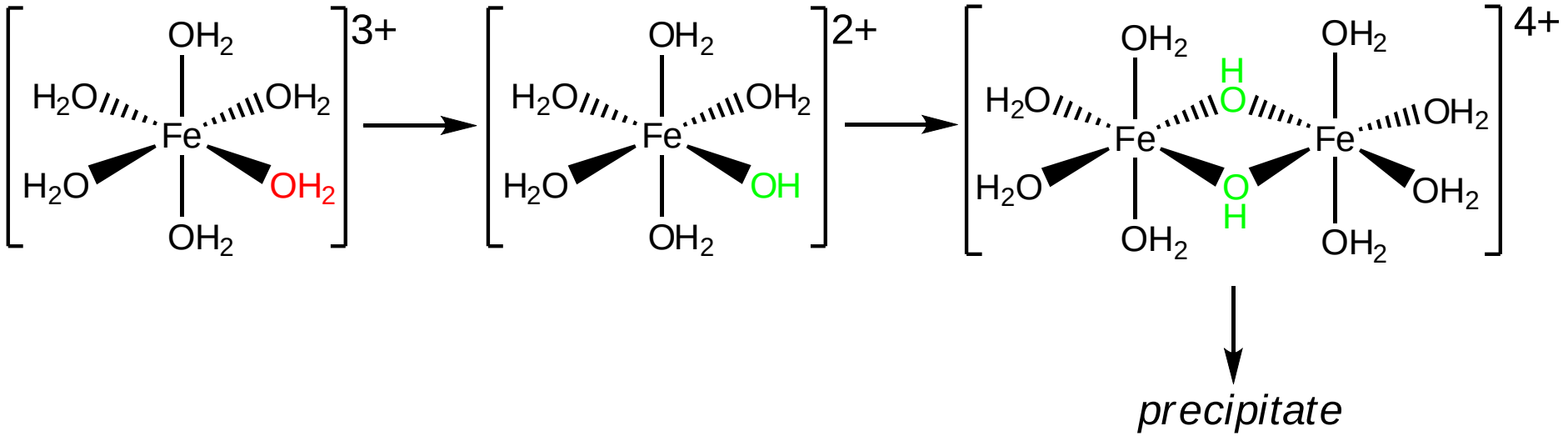
However, it does not act as a conventional Brønsted acid!
Not deprotonated at the hydroxide

Lewis acidity at boron results in the formation of an adduct weakening O–H bond in water



Poloxo- compounds

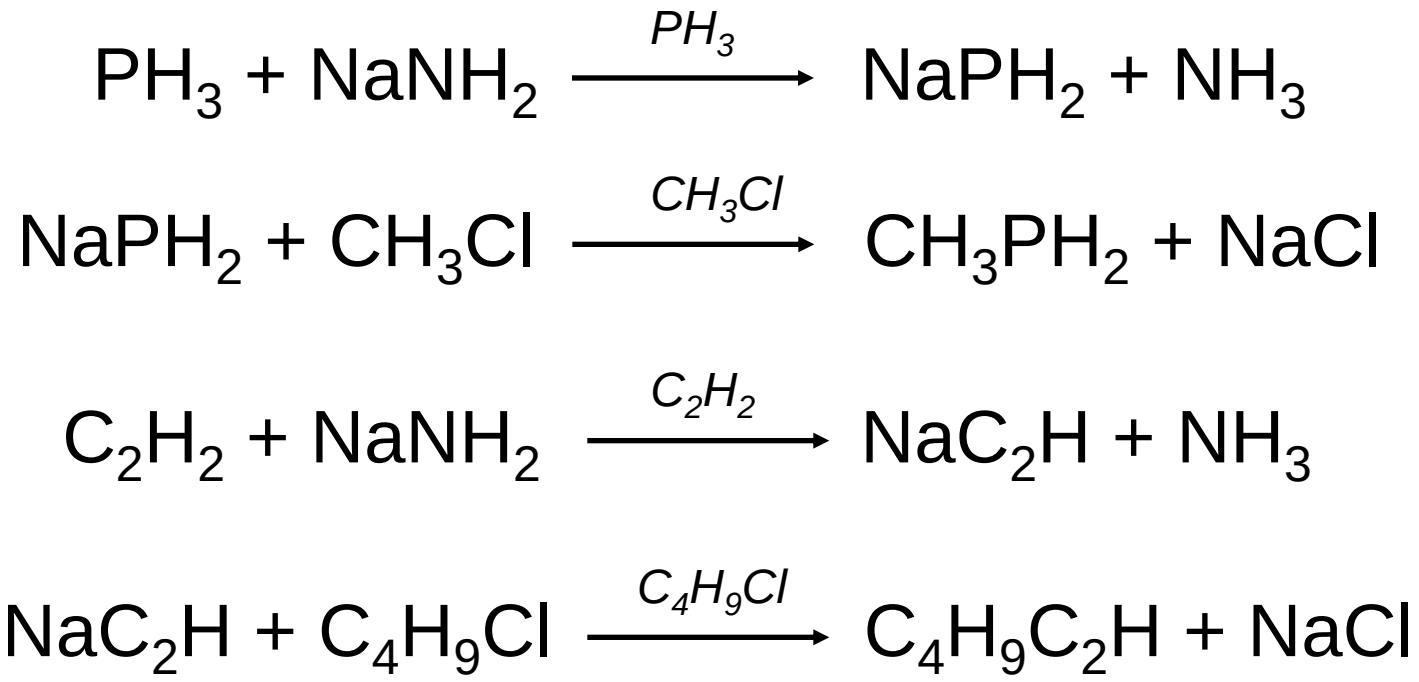
As the pH of a solution is increased the aqua ions of metals with basic or amphoteric oxides undergo polmerisation and precipitation



$$[Fe(OH_2)_6]^{3+}(aq) + (3 + n)H_2O \longrightarrow Fe(OH)_3 \bullet nH_2O + 3H_3O^+$$

$$[Al(OH_2)_6]^{3+}(aq) + (3 + n)H_2O \longrightarrow Al(OH)_3 \bullet nH_2O + 3H_3O^+$$

Syntheses using acid/base reactions in alternative solvents



From 2012 Prelims:

4. Answer *BOTH* part (a) and part (b).

(a) Account for the variation in the pK_a values of the acids given below. [7]

Acid:	HF	HCl	HBr	HI	$HClO_4$	$HClO_3$
pK_a	3.5	–7	–9	–11	–10	–3

(b) Account for each of the following observations: [3]

(i) Addition of SbF_5 to liquid HF forms a very strong "superacid".

(ii) CO_2 acts as a Brønsted acid in aqueous solution.

Acids, bases and solution equilibria

LECTURE 2

Lewis acid/base theory

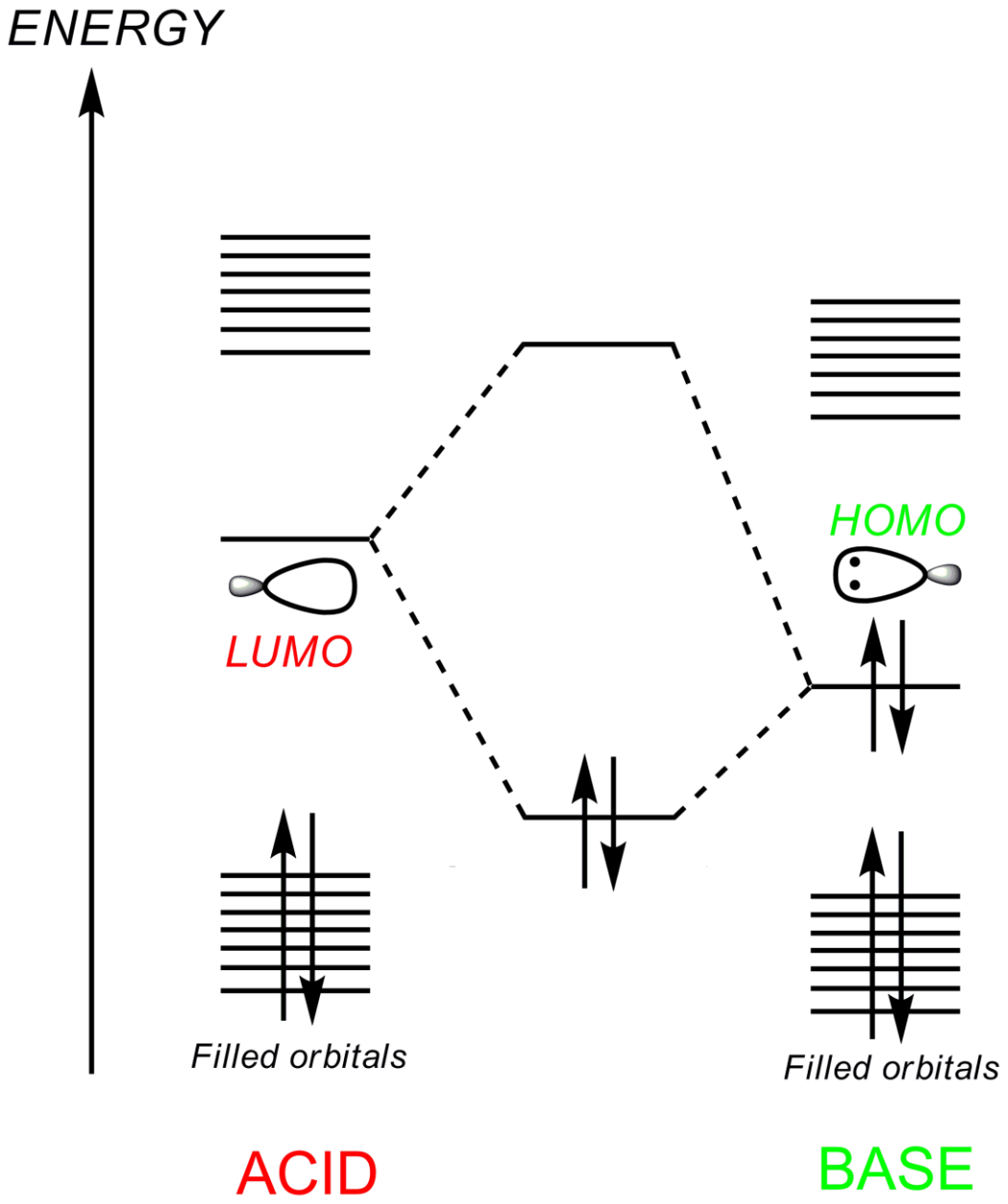
acid
e^- pair
acceptor

base
e^- pair
donor

adduct
complex

How do these interactions take place?

In addition to a base with a lone pair of electrons the acid must also have an empty orbital capable of interacting with the lone pair on the base. Electronically saturated complexes will not form an adduct.



Examples of Lewis acids

(1) H^+

A Brønsted acid exhibits Lewis acidity because it donates H^+, which in turn can accept a lone pair of electrons from a Lewis base.

Examples of Lewis acids

(2) M^{n+}

Metal cations

$$M^{n+} + x{:}B \longrightarrow [M(B)_x]^{n+}$$

acid
metal

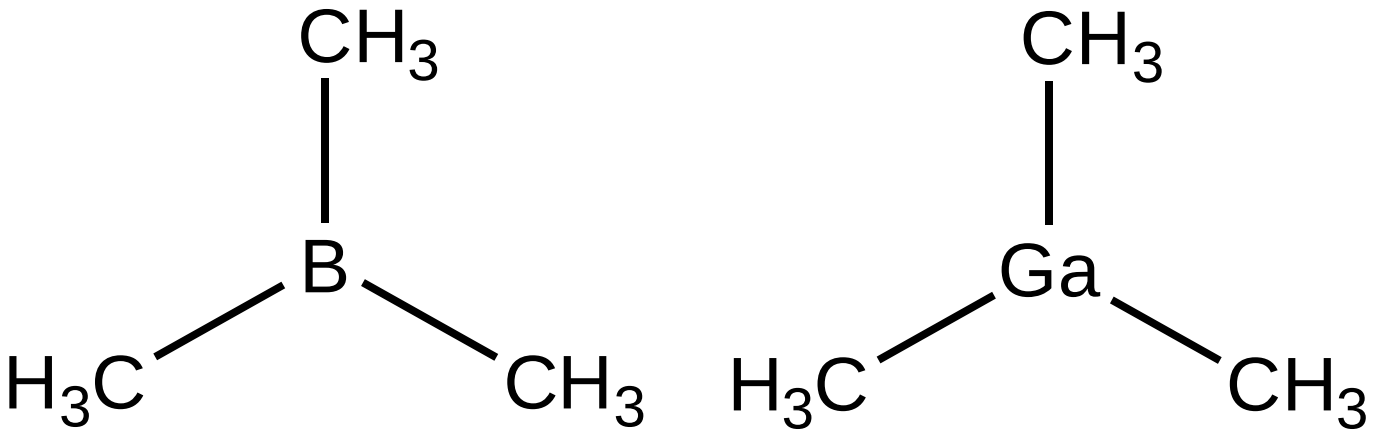
base
ligand

adduct
complex

e.g. aqua ions $[Fe(OH_2)_6]^{3+}$

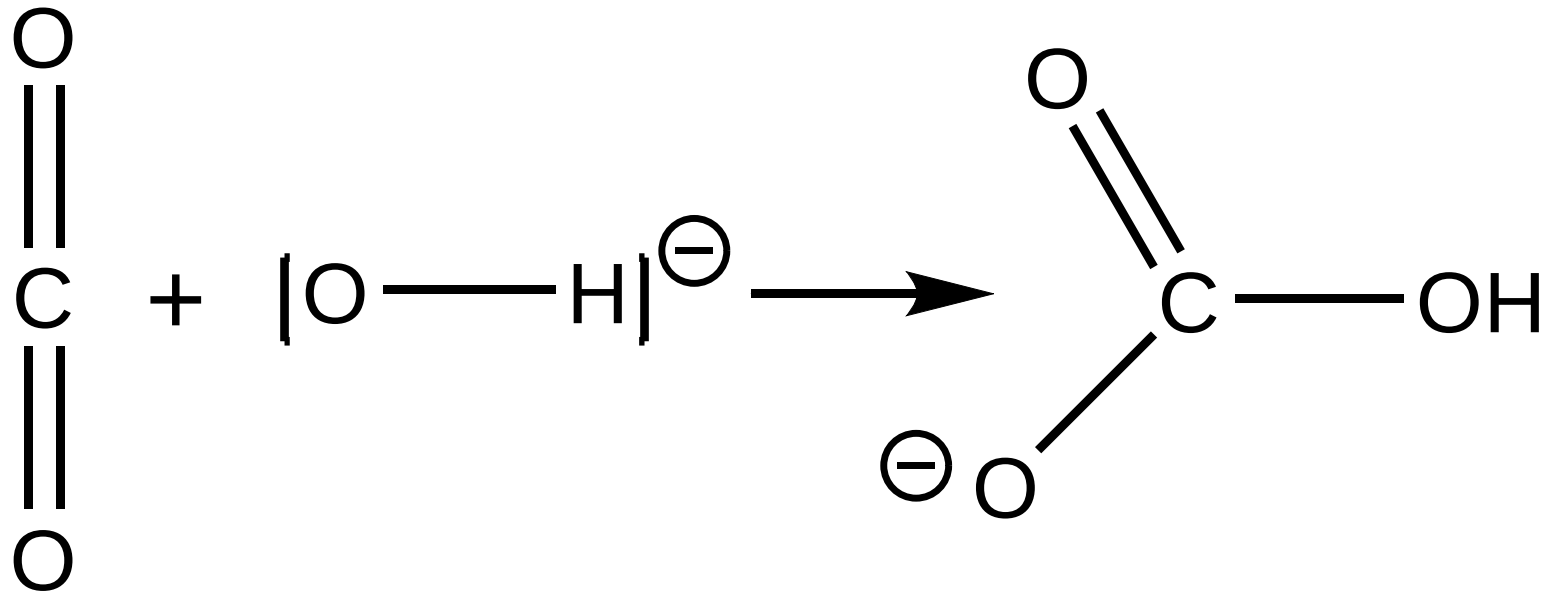
Examples of Lewis acids

(3) Main-group compounds with incomplete ‘octet’



Examples of Lewis acids

(4) Molecules that can arrange valence e^- to create a vacant orbital



Examples of Lewis acids

(5) Compounds of heavy p-block elements

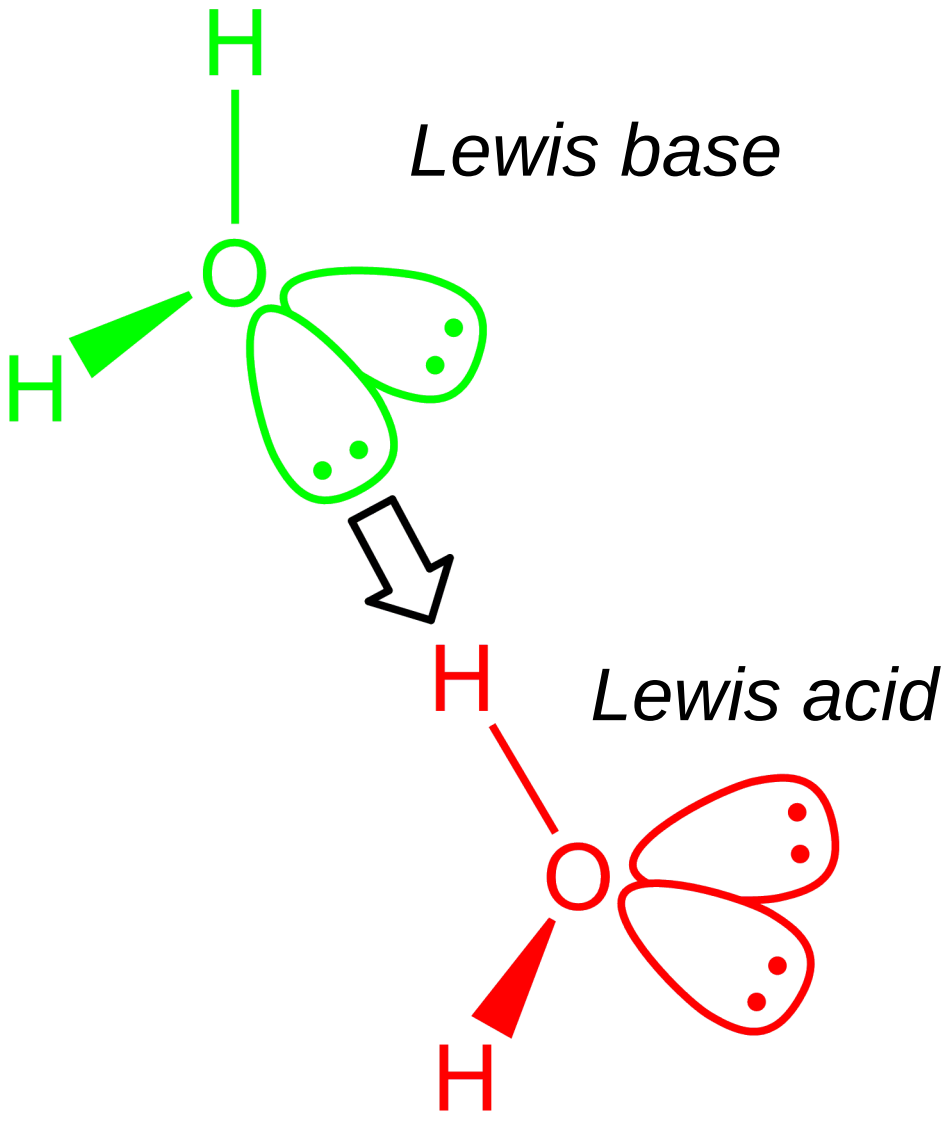
$$PF_5 + F^- \longrightarrow [PF_6]^-$$

$$SbCl_5 + Cl^- \longrightarrow [SbCl_6]^-$$

$$SiF_4 + 2F^- \longrightarrow [SiF_6]^{2-}$$

How Lewis acid/base chemistry influences structure (self acid-base interactions)

H-bonding

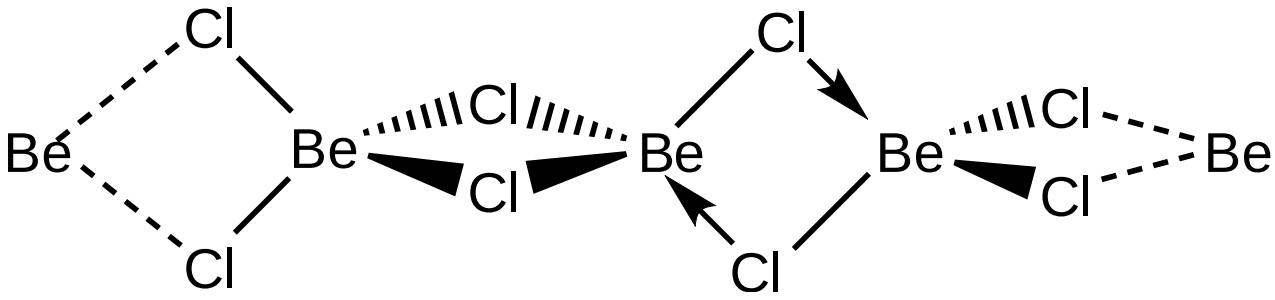


Lewis acid/base interactions have a strong influence on the physical properties of compounds

How Lewis acid/base chemistry influences structure (self acid-base interactions)

Structure of $BeCl_2$

Gas phase
High temperature

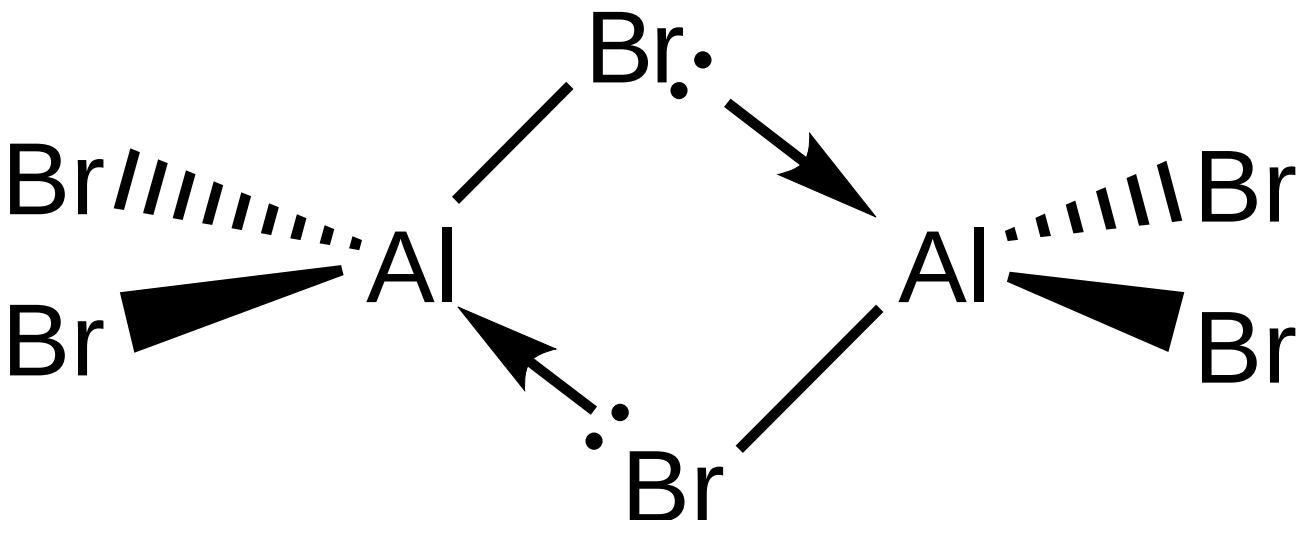


Solid state
One dimensional chain structure

How Lewis acid/base chemistry influences structure (self acid-base interactions)

Oligomerisation/Polymerisation

Structure of $AlBr_3$?



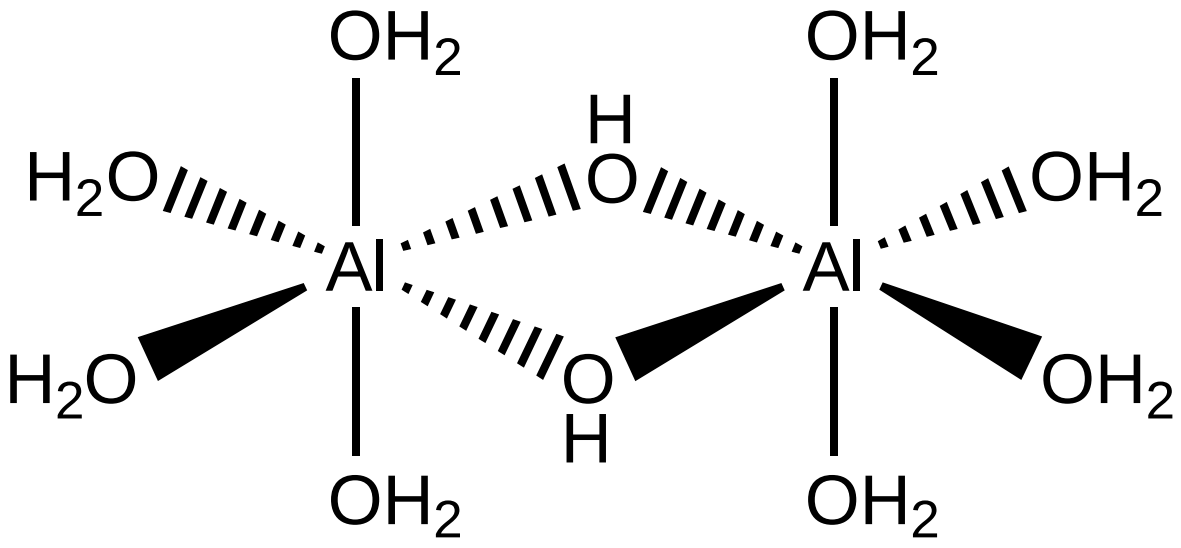
NOT monomeric $AlBr_3$!

How Lewis acid/base chemistry influences structure (self acid-base interactions)

Oligomerisation/Polymerisation

$$Al^{3+}_{(aq)} \xrightarrow{-H^+} [Al(OH_2)_5(OH)]^{2+} \longrightarrow \text{dimer}$$

Brønsted acid *Lewis acid*



Strength of Lewis acids and bases

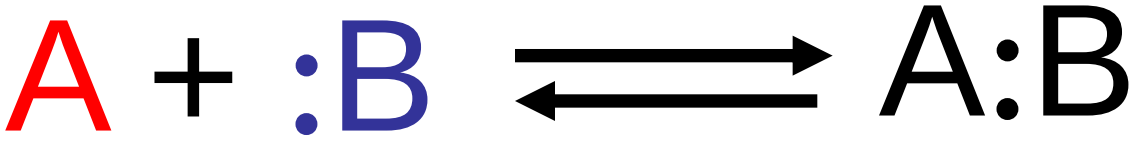
Factors:

1) Electronic properties
2) Structure

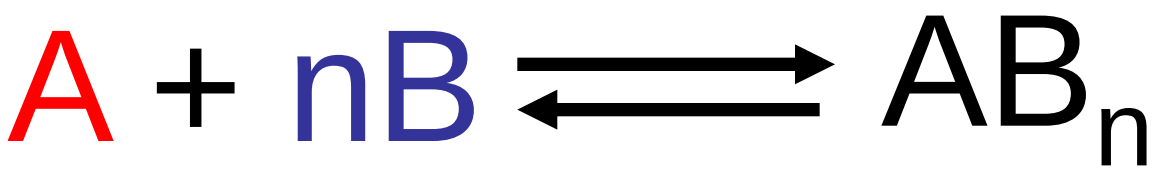
Techniques:

1) Spectroscopy
2) Electrochemistry
3) Calorimetry

Equilibrium constants



$$K_f = \frac{[AB]}{[A][B]}$$



$$\beta_n = \frac{[AB_n]}{[A][B]^n}$$

Experimental observations <u>in WATER</u>

Mg^{2+}

K_f: $F^- > Cl^- > Br^- > I^-$

Hg^{2+}

K_f: $I^- > Br^- > Cl^- > F^-$

Why???

HARD/SOFT interactions

Concept introduced by R. G. Pearson (1963)

Class a compounds = HARD

Small, Highly charged, Low polarizability

Class b compounds = SOFT

Large, Small or no charge, High polarizability

Observations by Ahrland, Chatt and Davies (1958)

Metal + Halide

Class a: $F^- > I^-$

Class b: $I^- > F^-$

TRUE FACT!
Well not really, but close enough

Examples

Metal + Halide

Class a: $F^- > I^-$

Class b: $I^- > F^-$

$$Al^{3+}(aq) + HgF^{+}(aq) \longrightarrow AlF^{2+}(aq) + Hg^{2+}(aq)$$

However,

$$AlI^{2+}(aq) + Hg^{2+}(aq) \longrightarrow Al^{3+}(aq) + HgI^{+}(aq)$$

Everyday examples

Goldschmidt classification of elements
Lithophiles: H-H
Chalcophiles: S-S

The tarnish on Al is OXIDE
The tarnish on Ag is SULPHIDE

Gold extracted as $[Au(CN)_2]^-$

HARD/SOFT

Hard likes hard

Soft likes soft

WHY???
Combination of Intrinsic
and Extrinsic effects

HARD ACIDS

H^+, Li^+, Ca^{2+}, Al^{3+}, Ti^{4+}

Non-polarisable, often small and highly charged

HARD BASES

F^-, O^{2-}, OH^-, CO_3^{2-}, SO_4^{2-}, NH_3

Non-polarisable, ions based on 2p elements

SOFT ACIDS

Cu^{+}, Ag^{+}, Cd^{2+}, Hg^{2+}, Tl^{+}

Large, small charge, polarisable

SOFT BASES

I^{-}, CN^{-}, RS^{-}, PR_3, CO

Typically involve elements from 3p and lower rows

Irving-Williams series

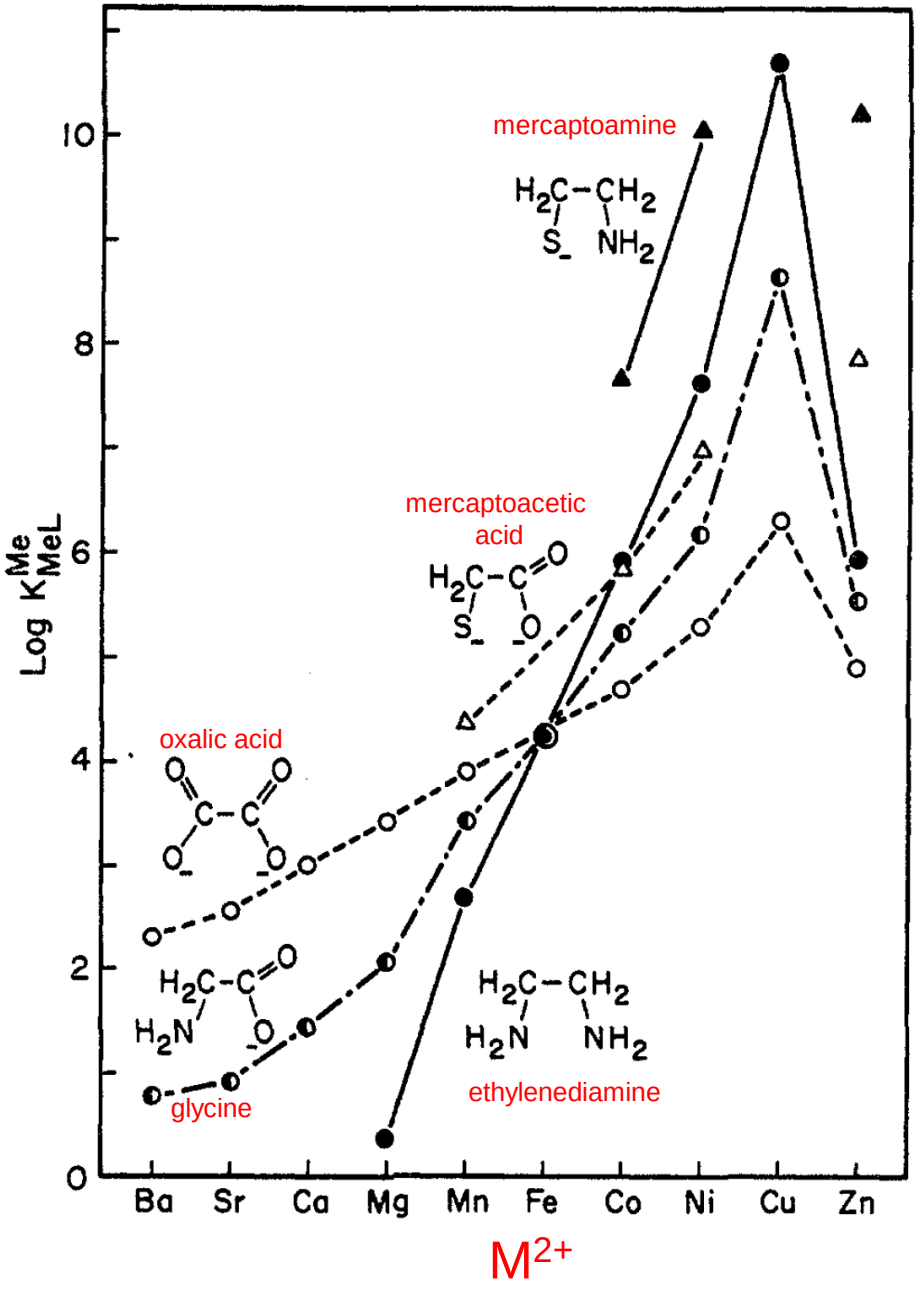
$$[M(H_2O)_n]^{2+} + L \rightleftharpoons [M(L)(H_2O)_{n-1}]^{2+} + H_2O$$

Ordering of K_f

$$Ba^{2+} < Ca^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} > Zn^{2+}$$

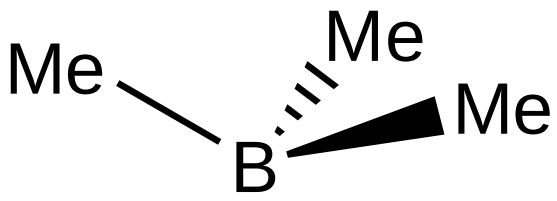
Approximately in order of decreasing r^+

Logarithms of the stability constants for the 1:1 complexes between Ba^{2+} through Zn^{2+} and the bidentate ligands oxalic acid, glycine, ethylenediamine, mercaptoacetic acid, and mercaptoethylamine.



Sigel, H.; McCormick, D. B. *Acc. Chem. Res.* **1970**, *3*, 201

Steric effects



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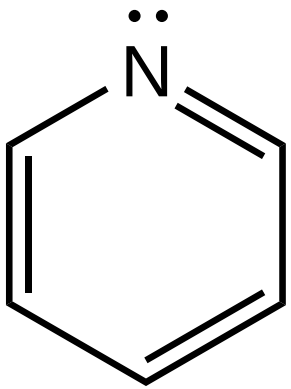
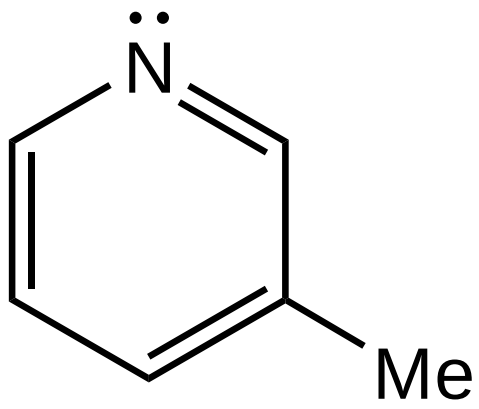


-71



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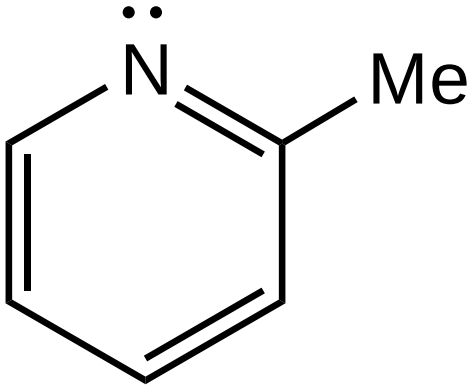
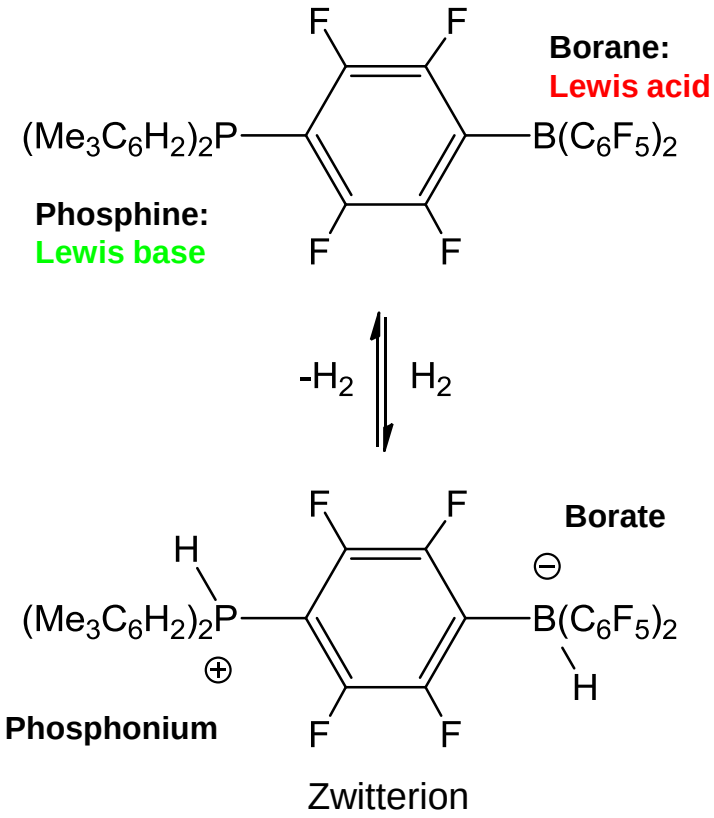


-42

$\Delta H_{rxn.}$/kJmol^{-1}

More steric effects: Frustrated Lewis Pairs



Zwitterion

Steric bulk prevents association of Lewis acidic and Lewis basic sites:

Unquenched reactivity!

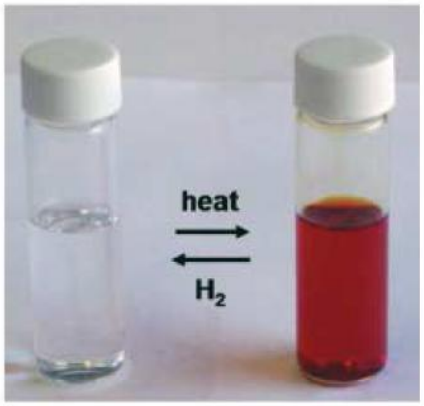
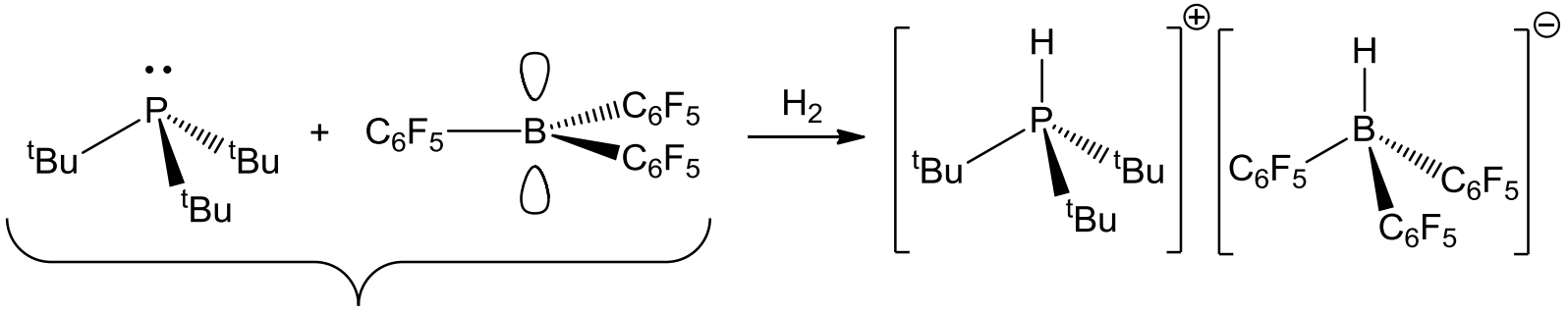


Figure form *Science* **2006**, *314*, 1124

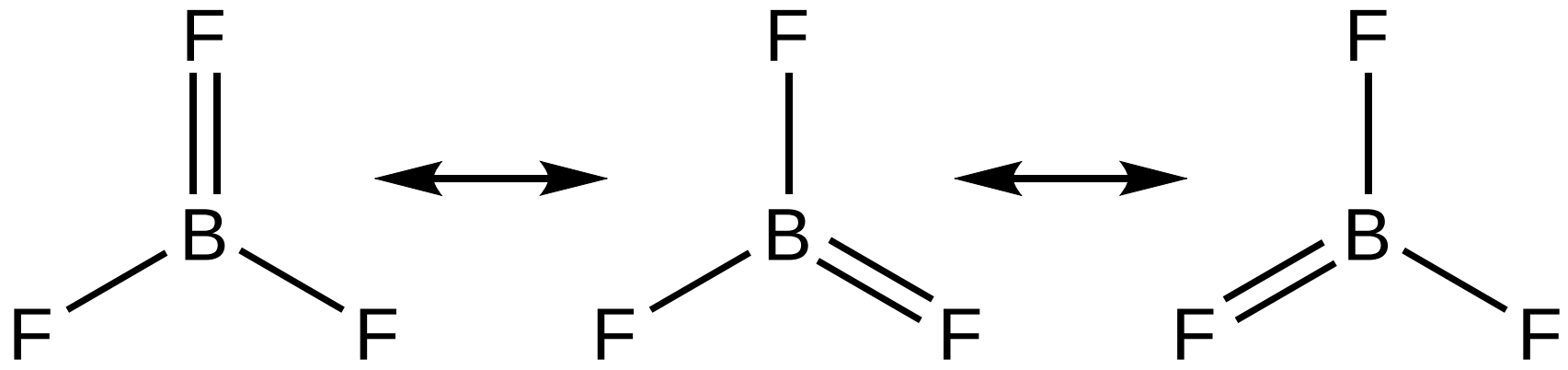


No adduct formation!

Acidity of BX_3

The order of thermodynamic stability of complexes of $:N(CH_3)_3$ with BX_3 is $BF_3<BCl_3<BBr_3$

Opposite of what one would expect using halogen electronegativites as an argument.



<u>π-orbital overlap between full halogen *p* orbitals and empty B 2*p* orbitals must be broken in order to form acid/base adduct</u>

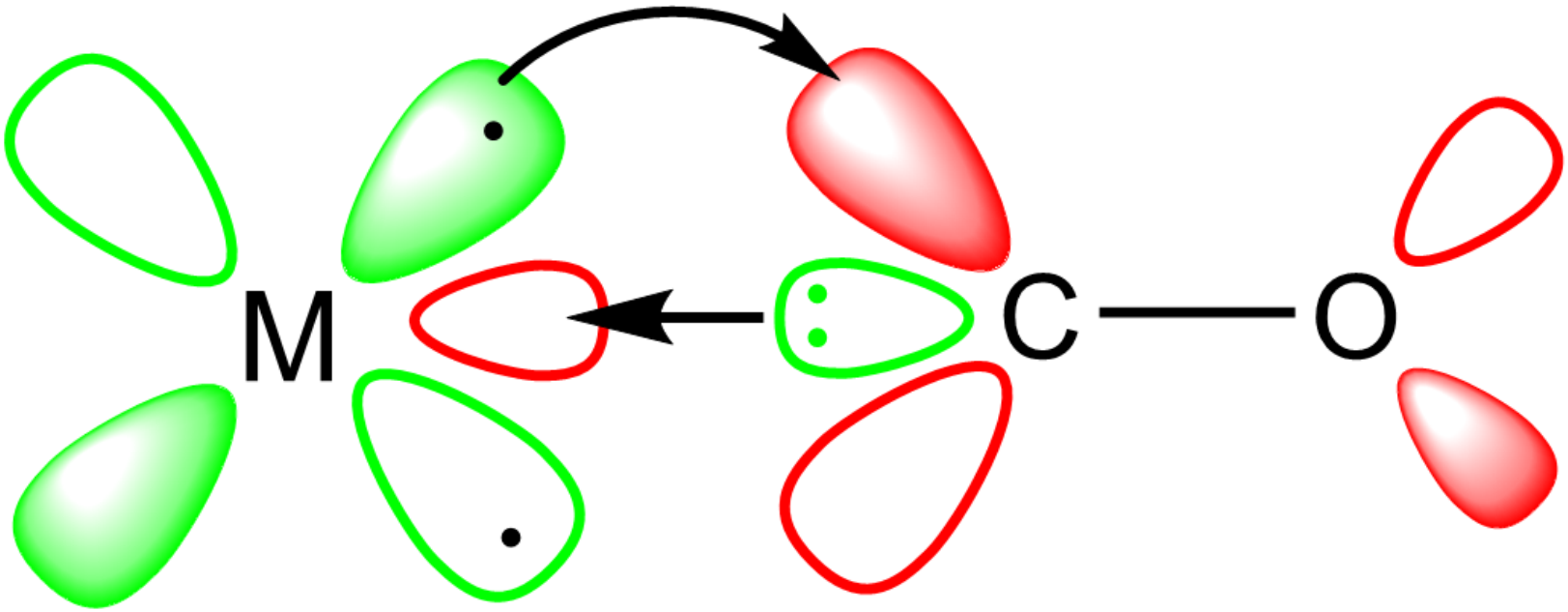
Trends in Lewis acidity

$SiI_4 < SiBr_4 < SiCl_4 < SiF_4$

but

$BF_3 < BCl_3 < BBr_3 < BI_4$

'Frontier' orbitals



LUMO Empty acceptor orbital

HOMO Donor orbital. Contains e^- pair

HARD-HARD

Ion-ion, ion-dipole
Non-polarlisable

SOFT-SOFT

Covalent bonding
Polarisable

HARD ACIDS

H^+, Li^+, Ca^{2+}, Al^{3+}, Ti^{4+}

Non-polarisable, often small and highly charged

HARD BASES

F^-, O^{2-}, OH^-, CO_3^{2-}, SO_4^{2-}, NH_3

Non-polarisable, ions based on 2p elements

SOFT ACIDS

Cu^{+}, Ag^{+}, Cd^{2+}, Hg^{2+}, Tl^{+}

Large, small charge, polarisable

SOFT BASES

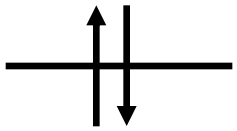
I^{-}, CN^{-}, RS^{-}, PR_3, CO

Typically involve elements from 3p and lower rows

HARD

LUMO

Hard base has
high-lying LUMO

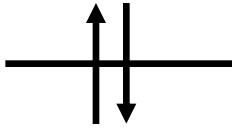
HOMO 

Hard base has
low-lying HOMO

SOFT

Soft base has
low-lying LUMO

 LUMO

 HOMO

Soft base has
high-lying HOMO

HARD-HARD

Ion-ion, ion-dipole
Non-polarlisable

SOFT-SOFT

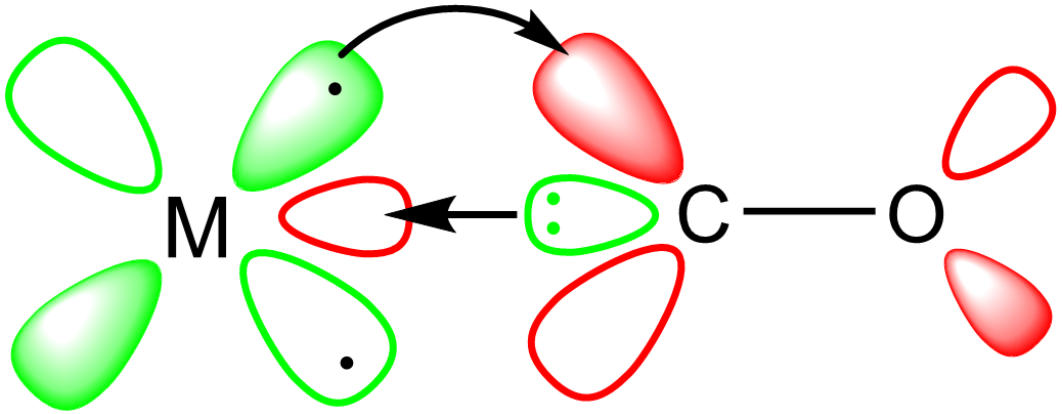
Covalent bonding
Polarisable

Interpretation of hardness and softness

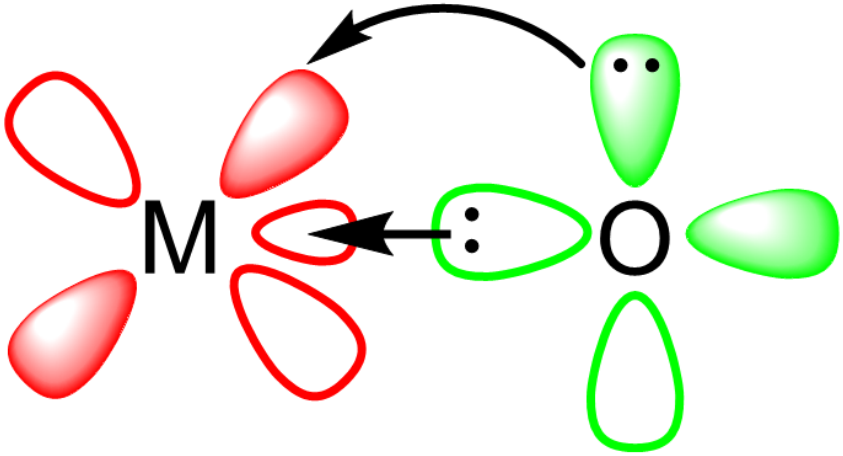
Hard acid-base interactions are predominantly electrostatic.

Soft acid-base interactions are predominantly covalent.

π-acidity; π-basicity



Stabilise soft Lewis acids (soft bases)



Stabilise hard Lewis acids (hard bases)

What reactions are we measuring?

$$Hg^{2+}(aq) + 4X^{-}(aq) \rightleftharpoons HgX_4^{2-}(aq)$$

X	***logK***
Cl	16
Br	22
I	30

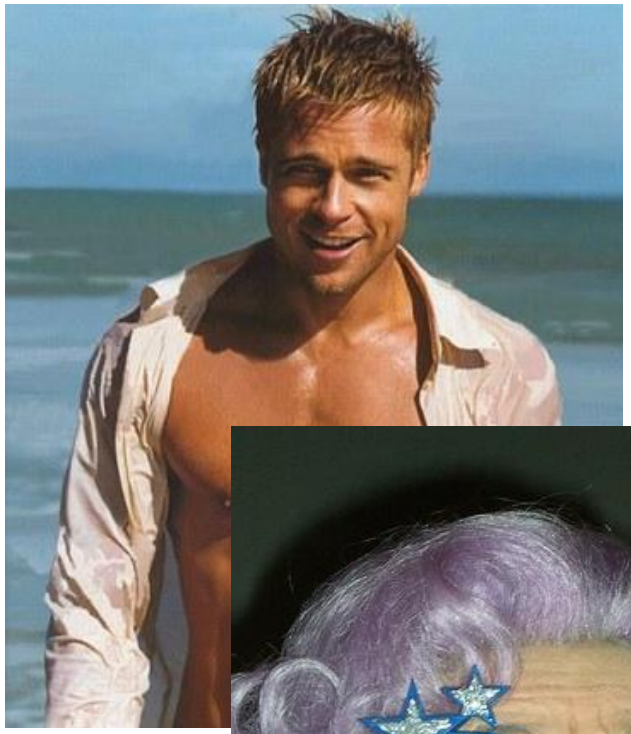
Gas phase

$$HgF_2 + BeI_2 \rightleftharpoons BeF_2 + HgI_2$$

ΔH (KJ/mol) for $MX_{2(g)} \rightarrow M_{(g)} + 2X_{(g)}$

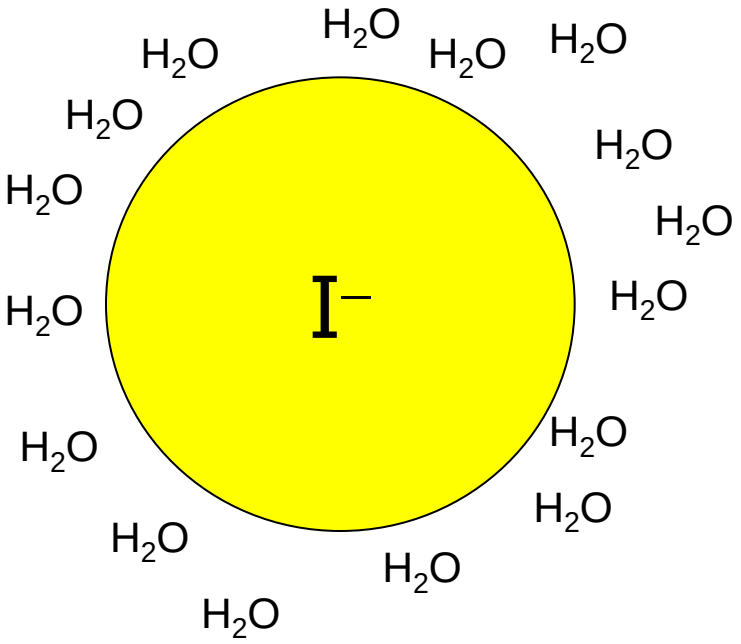
BeF_2	1264	***HgF_2***	536
BeI_2	578	***HgI_2***	291

Survivor HARD-SOFT



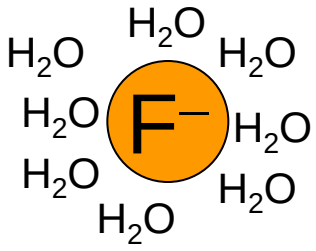
Competition!

$$HgF_{2(aq)} + I^-_{(aq)}$$



Very favourable

$$HgI_{2(aq)} + F^-_{(aq)}$$



Electron density is much higher
Stronger enthalpy of solvation

Effect of solvent

The solvent is not an innocent bystander… it is involved in the chemical process.

$$HgCl_2 + 2Br^- \rightleftharpoons HgBr_2 + 2Cl^-$$

Ω_m ← *GAS PHASE*

In H_2O →

Solvents

ε

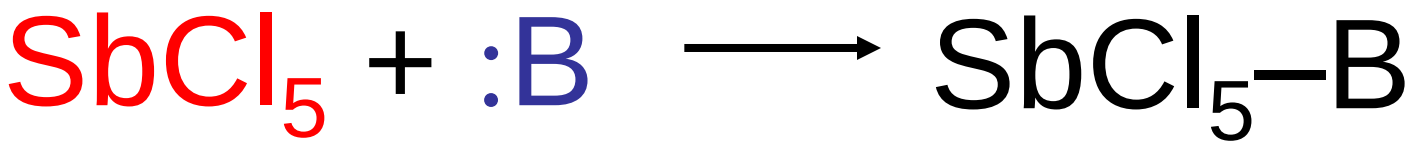
The solvent dielectric constant is a good guide for the importance of the solvent effect with charged species

However this is an oversimplification
Need to consider the solvent effect in terrms of Acid/Base interactions

Solvents are characterised by their DONOR numbers and ACCEPTOR numbers

DONOR NUMBER

Measured by taking a base :B and determining ΔH_{rxn} with $SbCl_5$ in $CH_2Cl\text{-}CH_2Cl$



DONOR NUMBER = $-\Delta H$ (kcal/mol)

ACCEPTOR NUMBER

Measured NMR chemical shifts of ^{31}P in $Et_3P=O$ (triethylphosphine oxide) in the pure solvent

$Et_3P=O$

Arbitrary scale:

Hexane = 0

$SbCl_5$ = 100

SOLVENT	***DN***	***AN***	***ε***
Pyridine	33.1	14.2	12.3
DMSO	29.8	19.3	45
Diethylether	19.2	3.9	4.3
H_2O	18	54.8	81.7
Ethanoic acid	-	52.9	6.2
Acetone	17	12.5	20.7
Acetonitrile	14.1	19.3	36
Benzene	0.1	8.2	2.3
CCl_4	-	8.6	2.2
$SbCl_5$	-	100	-
CF_3COOH	-	105.3	-

SOLVENT	DONOR NUMBER	ACCEPTOR NUMBER
Acetic acid	-	52.9
Acetic anhydride	10.5	-
Acetone	17.0	12.5
Acetonitrile	14.1	19.3
Acetyl chloride	0.7	-
Antimony pentachloride	-	100
Benzene	0.1	8.2
Carbon tetrachloride	-	8.6
Chloroform	-	23.1
Dichloromethane	-	20.4
Diethylether	19.2	3.9
Dimetylsulfoxide (DMSO)	29.8	19.3
Dioxane	14.8	10.8
Ethanol	19.0	37.1
Ethyl acetate	17.1	-
Formamide	-	39.8
Hexamethylphosphorotriamide (HMPA)	38.8	10.6
Methanol	20.0	41.3
Methyl acetate	16.5	-
Methylsulfonic acid	-	126.1
Nitrobenzene	4.4	14.8
Nitromethane	2.7	20.5
Phosphorus oxychloride	11.7	-
Propanol	18.0	33.5
Pyridine	33.1	14.2
Tetrahydrofuran (THF)	20.0	8.0

Drago + Wayland

For:

$$A_{(g)} + B_{(g)} \longrightarrow AB_{(g)}$$

$$-\Delta H = E_A E_B + C_A C_B$$

$E_{A,\,B}$ = ionic susceptibility

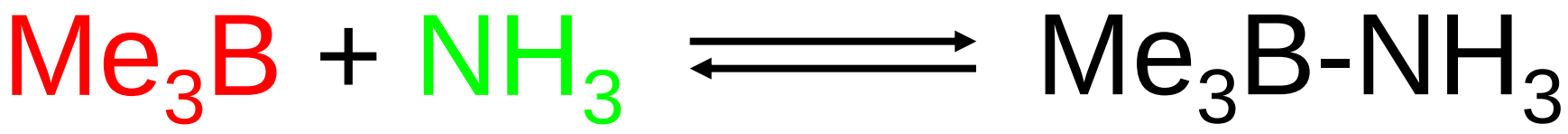
$C_{A,\,B}$ = covalent susceptibility

Drago – Wayland parametres

	E	C
acids		
$SbCl_5$	15.1	10.5
BMe_3	12.6	3.48
SO_2	1.88	1.65
Iodine	2.05	2.05
bases		
NH_3	2.78	7.08
Benzene	0.23	2.9
Pyridine	1.17	6.40
Methylamine	1.30	5.88

Drago-Weyland parametres reflect electrostatic (E) and covalent (C) factors, but not solvation

Using the Drago – Wayland equation



$$\Delta H = -(E_A E_B + C_A C_B)$$

$$\Delta H = -[(12.6 \times 2.78) + (3.48 \times 7.08)]$$

$$\underline{\Delta H = -59.7 \text{ kJ/mol}}$$

Experimentally: $\Delta H = -57.5$ kJ/mol

Superacids

A Lewis acid can be used to ‘boost’ the acidity of a Brønsted acid

$$2HF + SbF_5 \longrightarrow \underline{[H_2F]^+} + [SbF_6]^-$$

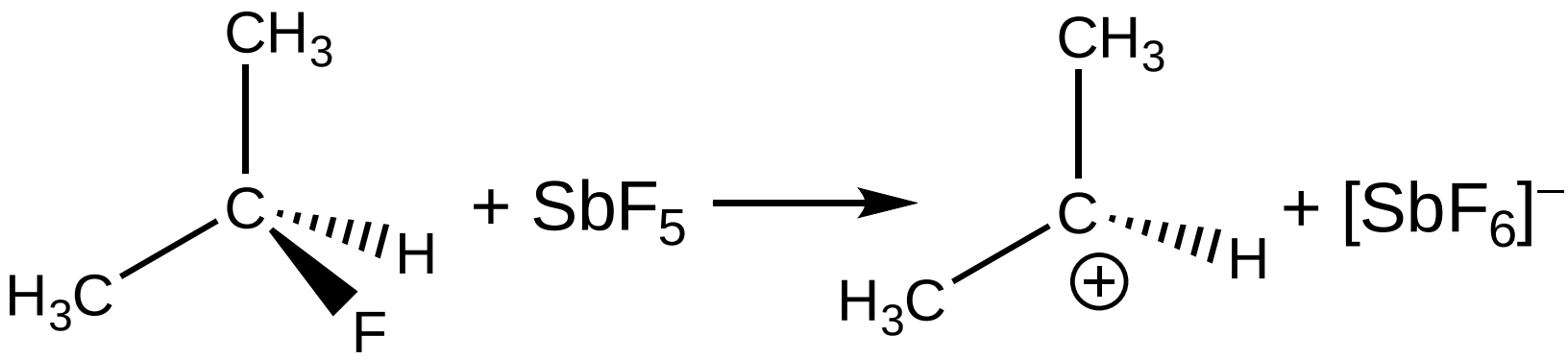
and…

$$2HSO_3F + SbF_5 \longrightarrow$$

$$\underline{[H_2SO_3F]^+} + [FSO_3\text{-}SbF_5]^-$$

Magic acid

Generation of reactive carbocations



Di-Xenon

$$XeF^{+} + HF/SbF_5 \xrightarrow{Xe} [Xe_2]^{+} + [Sb_4F_{21}]^{-}$$

ACID-BASE THEORY: CONCEPTS TO REMEMBER

Brønsted-Lowry acids/bases: proton transfer; pK_a

Proton affinity; Relative proton affinity. Solvent effect.

Pauling's rules for oxo-acids.

Hard-soft interactions. Effect of solvent.

Measures of solvent polarity and/or donor/acceptor ability.

From 2012 Prelims:

4. Answer *BOTH* part (a) and part (b).

(a) Account for the variation in the pK_a values of the acids given below. [7]

Acid:	HF	HCl	HBr	HI	$HClO_4$	$HClO_3$
pK_a	3.5	–7	–9	–11	–10	–3

(b) Account for each of the following observations: [3]

(i) Addition of SbF_5 to liquid HF forms a very strong "superacid".

(ii) CO_2 acts as a Brønsted acid in aqueous solution.

Acids, bases and solution equilibria

LECTURE 3

Electron transfer

The simplest chemical reaction:

$$X^{m} + Y^{n} \longrightarrow X^{m-1} + Y^{n+1}$$

X = oxidant
Y = reductant
m, n are formal oxidation states before reaction

e.g.:

$$Fe^{3+}(aq) + Cr^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Cr^{3+}(aq)$$

Atom transfer

$$XO + Y \longrightarrow X + YO$$

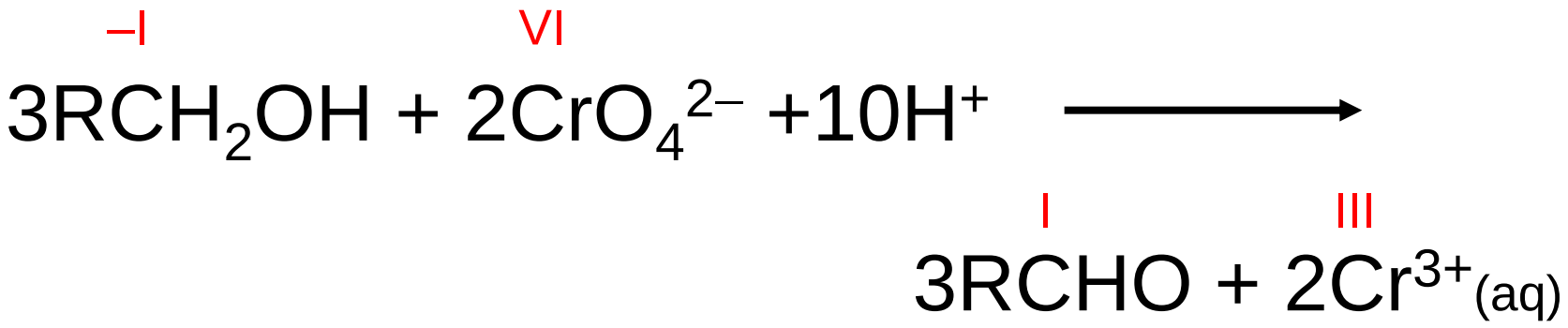
$$X + YH_2 \longrightarrow XH_2 + Y$$

e.g.:

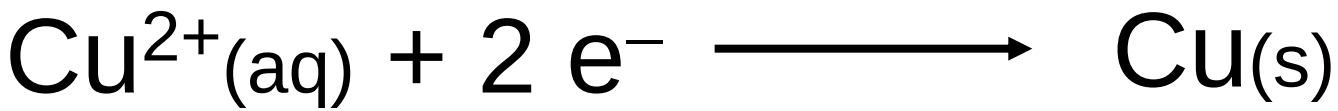
$$\overset{V}{NO_3^-} + \overset{IV}{SO_3^{2-}} \longrightarrow \overset{III}{NO_2^-} + \overset{VI}{SO_4^{2-}}$$

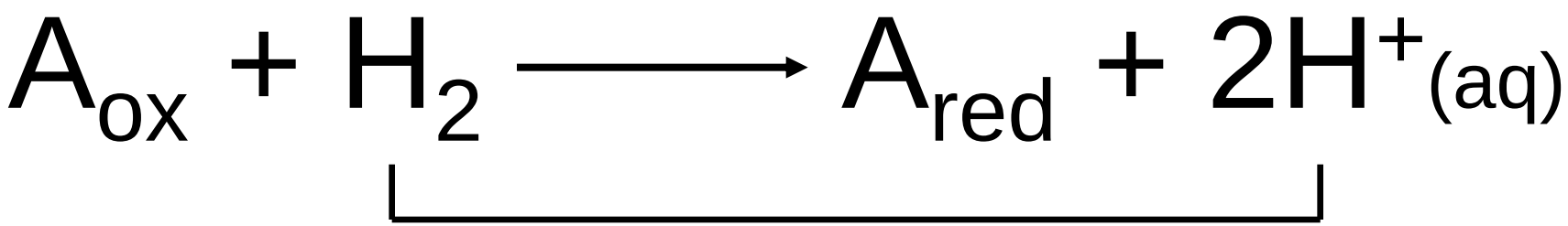
$$\overset{II}{CO} + \overset{I}{H_2O} \longrightarrow \overset{IV}{CO_2} + \overset{0}{H_2}$$

Redox reactions occur entirely in solution…



… or at the interface; e.g. an electrode





1 atm H_2

"1 M" H^+ (i.e. pH = 0)

Standard Hydrogen electron

$$K = \frac{[A_{red}][H^+]^2}{[A_{ox}][H_2]}$$

← $p(H_2)$

Van't Hoff equation

$$K = 10^{(-\Delta G^{\ominus}/2.3RT)}$$

R = universal gas cte.
8.314472(15) $JK^{-1}mol^{-1}$

Write as Half-reactions

Electron is “common currency”…

$$A_{ox} + 2e^- \longrightarrow A_{red} \quad (1)$$

$$2H^+_{aq} + 2e^- \longrightarrow 2H_2 \quad (2)$$

overall reaction is: **1 – 2**

$$\Delta G_{rxn}^{o} = \Delta G_A^{\ominus} - \Delta G_H^{\ominus}$$

By definition $\Delta G_H^\ominus = 0$

$$\Delta G_{rxn}^\ominus = \Delta G_A^\ominus$$

$$\Delta G_{rxn}^\ominus = - n F E^\ominus$$

so...

$$E^\ominus = \frac{2.3RT}{nF} \log K$$

$$A_{ox} + B_{red} \overset{K_{AB}}{\rightleftharpoons} A_{red} + B_{ox}$$

The two half-reactions are:

$$A_{ox} + ne^- \rightleftharpoons A_{red} \qquad E^{\ominus}_A$$

$$B_{ox} + ne^- \rightleftharpoons B_{red} \qquad E^{\ominus}_B$$

$$\log K_{AB} = \frac{n\,F}{2.3RT}\,(E^{\ominus}_A - E^{\ominus}_B)$$

Generalise for any system…

$$\Delta G = \Delta G^{\ominus} + 2.3RT\log Q$$

Q = reaction quotient

$$E = E^{\ominus} - \frac{2.3RT}{n\,F} \log \frac{[A_{red}]}{[A_{ox}]} =$$

$$= E^{\ominus} + \frac{2.3RT}{n\,F} \log \frac{[A_{ox}]}{[A_{red}]}$$

Nernst equation

At 298K:

$$E^{\ominus} + \frac{0.059}{n} \log \frac{[A_{ox}]}{[A_{red}]}$$

We can now calculate equilibrium constants and direction of reaction for ANY redox reaction

But first consider 'simple' electron-transfer reactions

To note:

1) $nE^{\ominus}$ $\left(= -\frac{\Delta G^{\ominus}}{F}\right)$

VOLT EQUIVALENT

2) Convention of direction of half-reaction

$$A_{ox} + ne^{-} \rightleftharpoons A_{red}$$

Always <u>REDUCTION POTENTIAL</u>

Observe:

$$I.E._1 < I.E._2 < I.E._3 < \ldots$$

However trends in $E^{\ominus}$ vary

OXIDATION STATES CONTROLLED BY CHEMISTRY

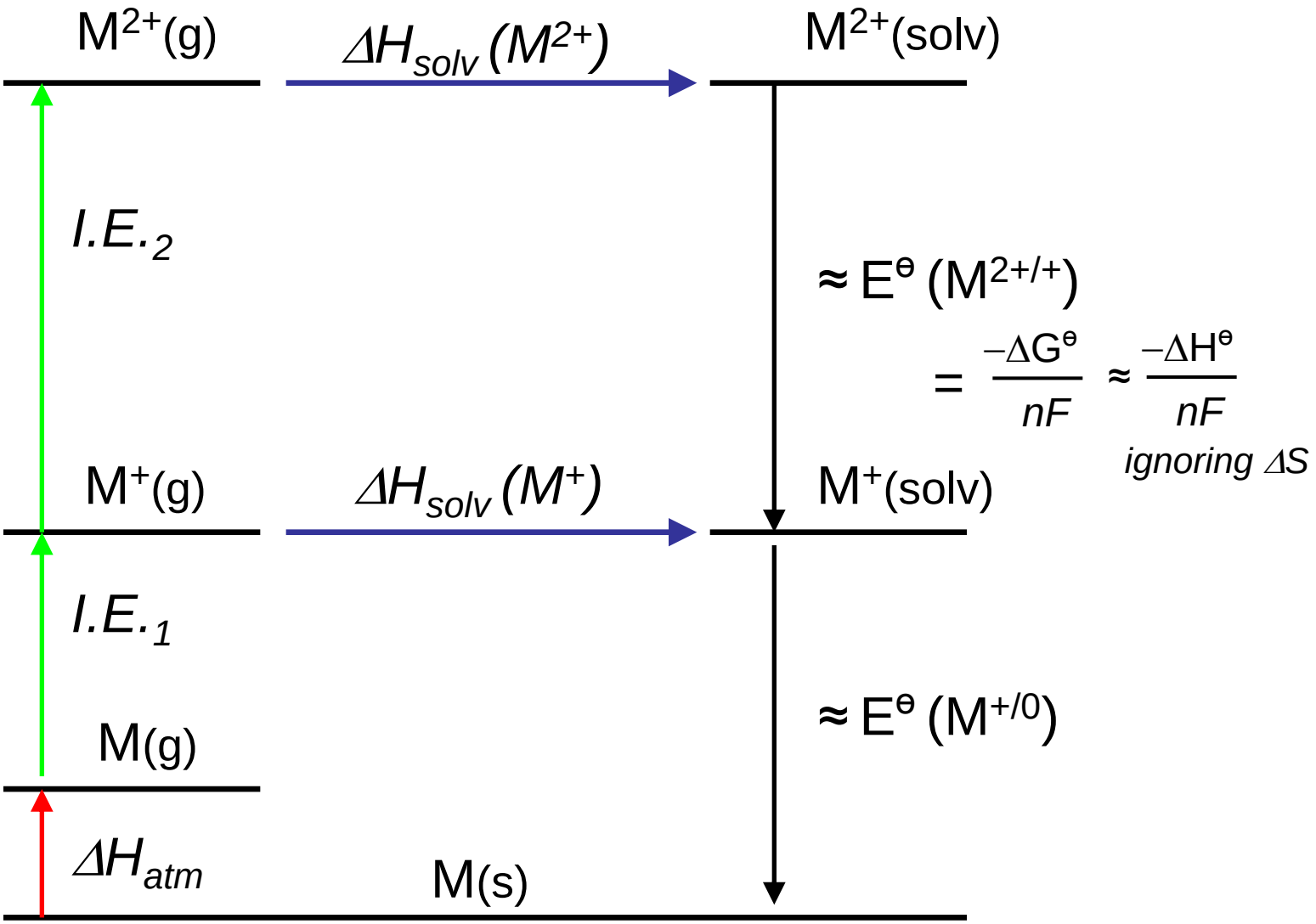
$$\Delta H_{atm}, \Delta H_{complexation}$$

e.g. solvation

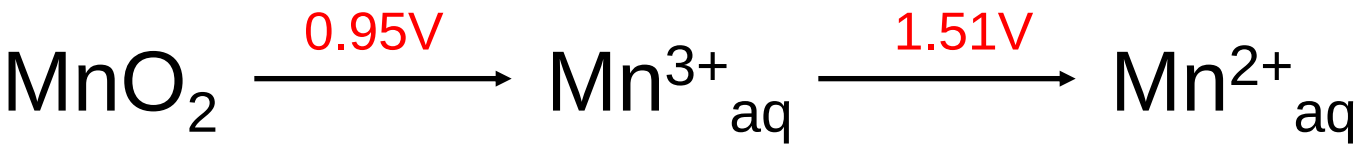
FROM PRELIMS 2006:

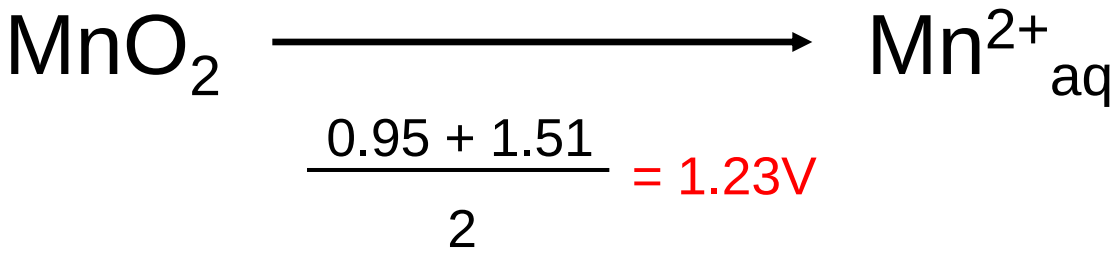
(iii) Account for the variation in the standard electrode potentials $E^{\ominus}(M^{+}/M)$ / V of the Group I metals, as tabulated below: **[4]**

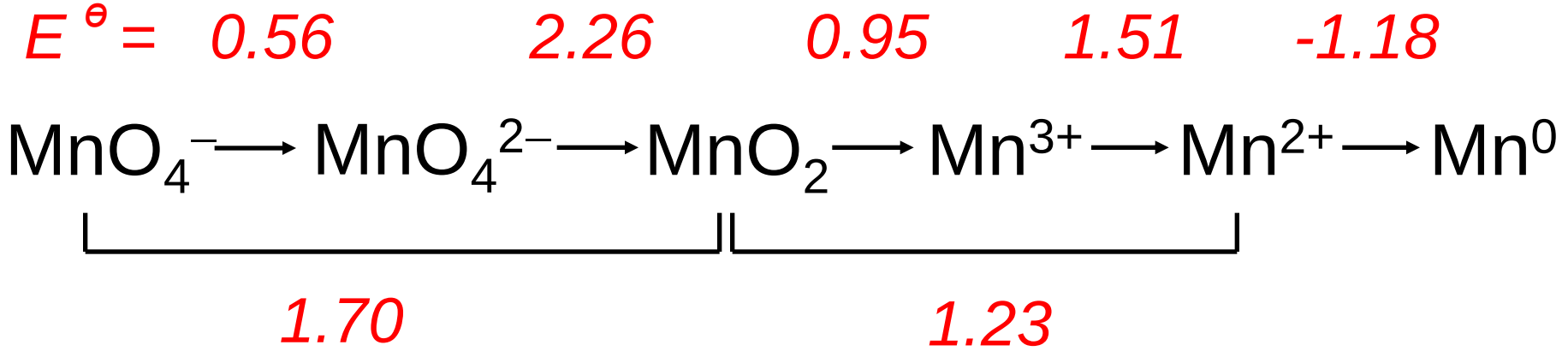
Li	Na	K	Rb	Cs
-3.03	-2.71	-2.93	-2.94	-3.02


M2+(g)
ΔHsolv (M2+)
M2+(solv)
I.E.2
≈ Eθ (M2+/+)
= −ΔGθ / nF ≈ −ΔHθ / nF
ignoring ΔS
M+(g)
ΔHsolv (M+)
M+(solv)
I.E.1
≈ Eθ (M+/0)
M(g)
ΔHatm
M(s)

Lattimer diagrams







$$E = \frac{\Sigma(nE^{\ominus})}{\Sigma n}$$

$$E^{\ominus}_{MnO_4^-/Mn^{2+}}$$

$$\frac{0.56 + (2 \times 2.26) + 0.95 + 1.51}{5}$$

$$= 1.51\ V$$

Observe:

Redox dispropotionation:

There are numerous examples in which a particular oxidation state is inherently unstable.

Let's consider a generic case, M^{n+}

$$2M^{n+} \xrightarrow{K_{disp}} M^{(n+1)+} + M^{(n-1)+}$$

The two half reactions are:

$$M^{n+} + e^- \longrightarrow M^{(n-1)+} \quad E^{\ominus}_1$$

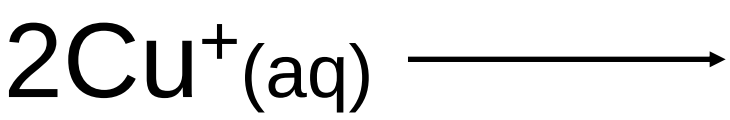
$$M^{(n+1)+} + e^- \longrightarrow M^{n+} \quad E^{\ominus}_2$$

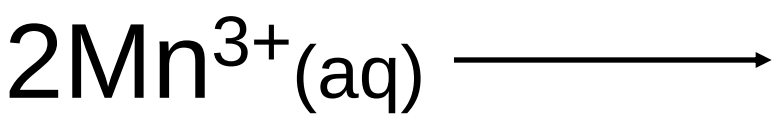
$$\log K_{disp} = \frac{n\,F}{2.3RT}\,(E^{\ominus}_1 - E^{\ominus}_2)$$

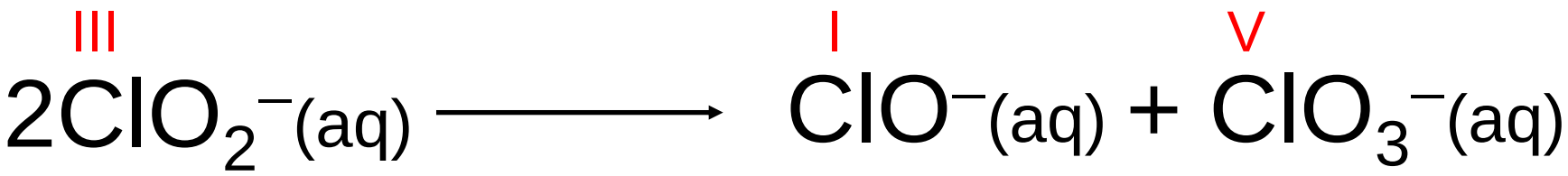
M^{n+} is unstable

if $E^{\ominus}_{1} > E^{\ominus}_{2}$

Examples







These also include main-group species with an odd number of electrons Al^{I}, P^{IV}, S^{V}, S^{III}, Pb^{III} etc. and T.M. compounds in +1 oxidation state

Let's consider Cu^+

$$2Cu^+_{(aq)} \xrightarrow{K_{disp}} 2Cu^+_{(aq)} + Cu_{(s)}$$

The two half reactions are:

$$Cu^+_{(aq)} + e^- \longrightarrow Cu_{(s)} \qquad E^\ominus = 0.52V$$

$$Cu^{2+}_{(aq)} + e^- \longrightarrow Cu^+_{(aq)} \qquad E^\ominus = 0.15V$$

$$\log K_{disp} = 16.9\,(0.52 - 0.15)$$

$$K_{disp} = 10^{6.3}$$

Stability of $Mn^{3+}_{(aq)}$

$$2Mn^{3+}_{(aq)} \longrightarrow Mn^{2+}_{(aq)} + MnO_{2(aq)} + 4H^{+}$$

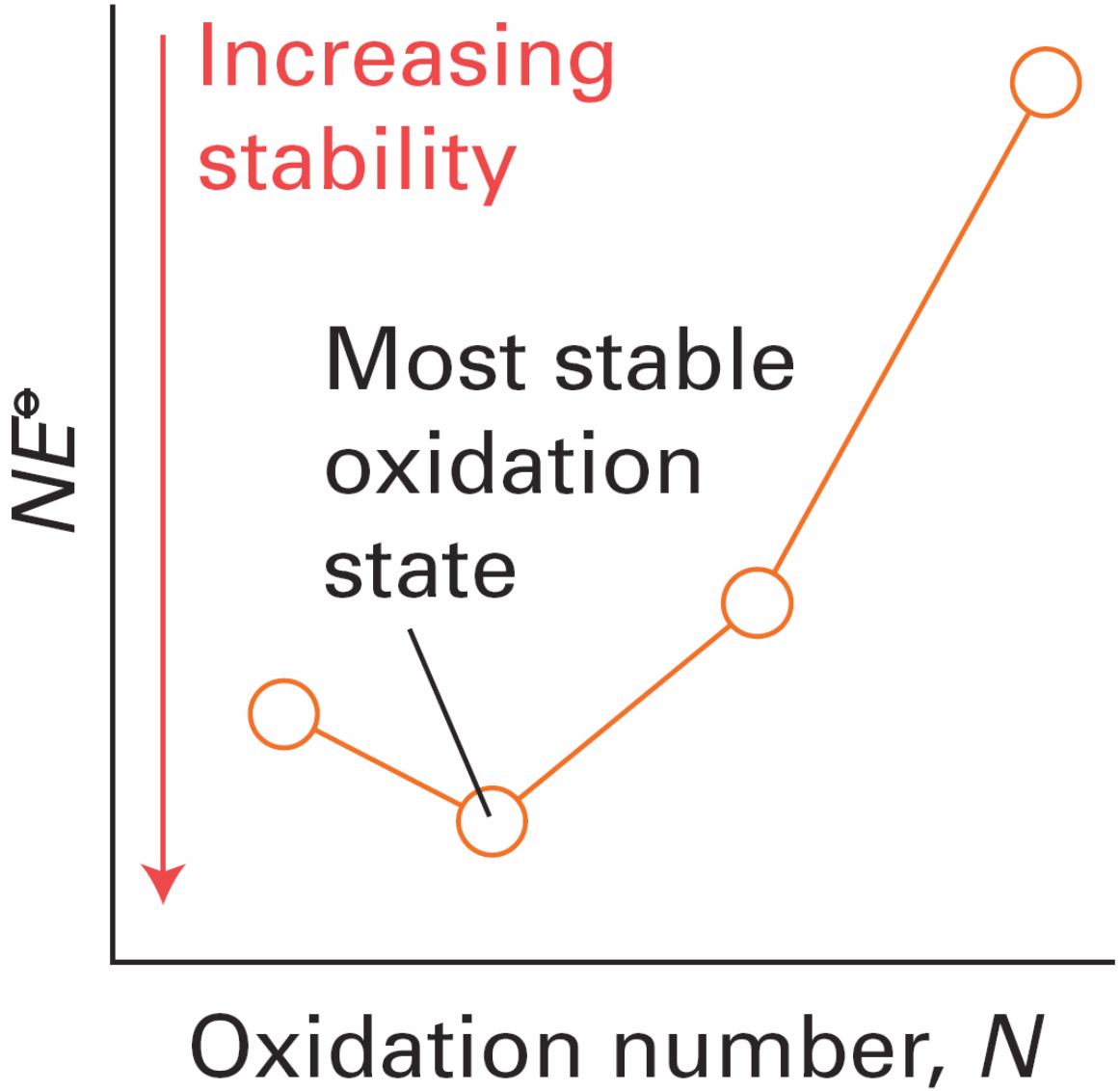
The two half reactions are:

$$Mn^{3+}_{(aq)} \longrightarrow Mn^{2+}_{(aq)} \qquad E^{\ominus} = 1.51V$$

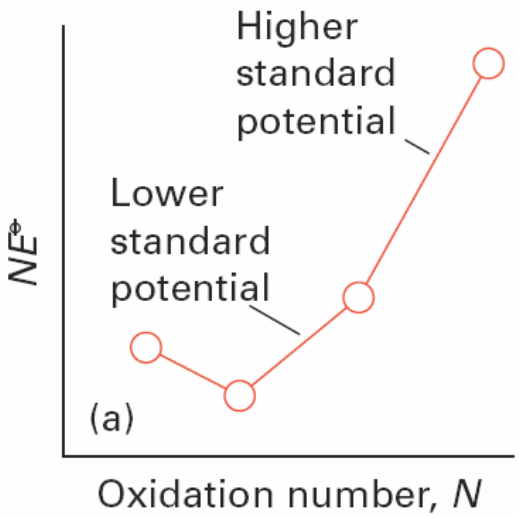
$$MnO_{2(s)} + 4H^{+} \longrightarrow Mn^{3+}_{(aq)} \qquad E^{\ominus} = 0.95V$$

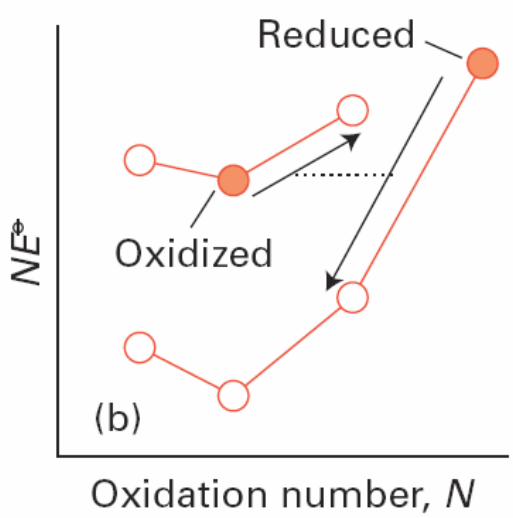
$$\Delta G^{\ominus} = -(1.51\text{-}0.95)\,F = -27 \text{ kJ/mol}$$

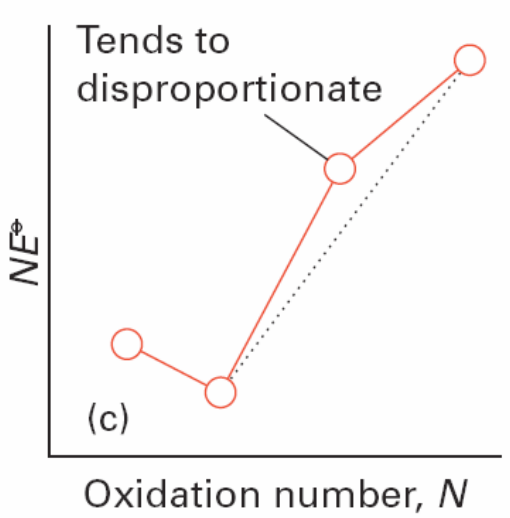
The Frost diagram

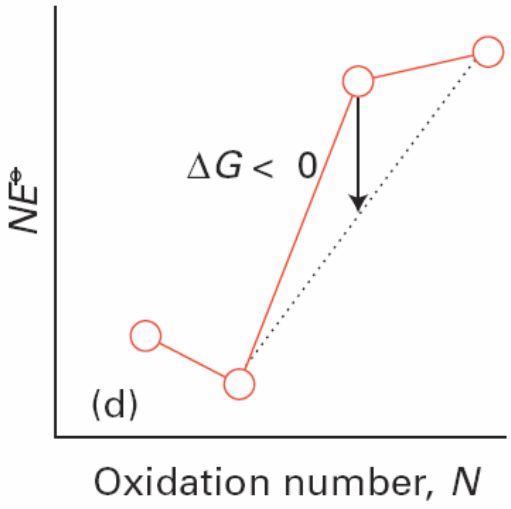


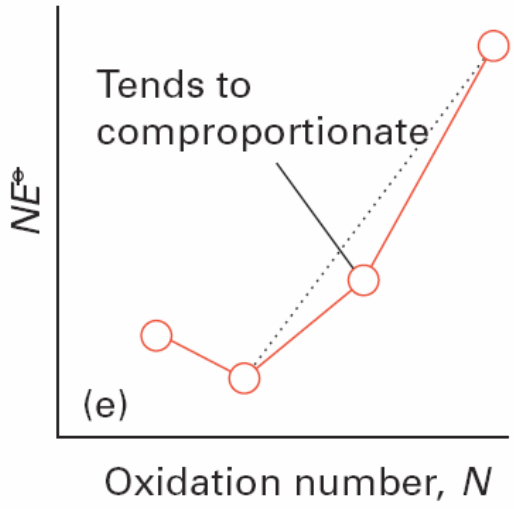
Interpreting Frost diagrams

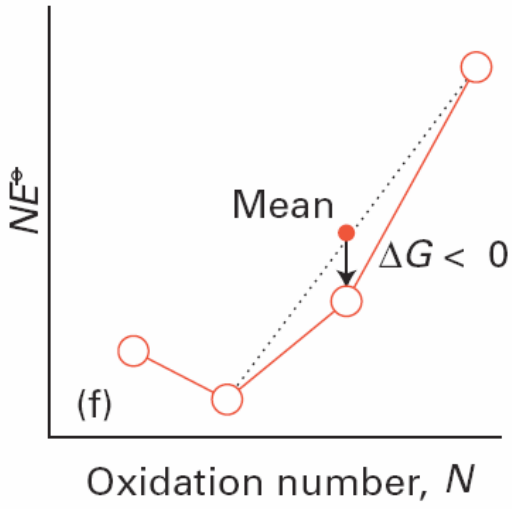




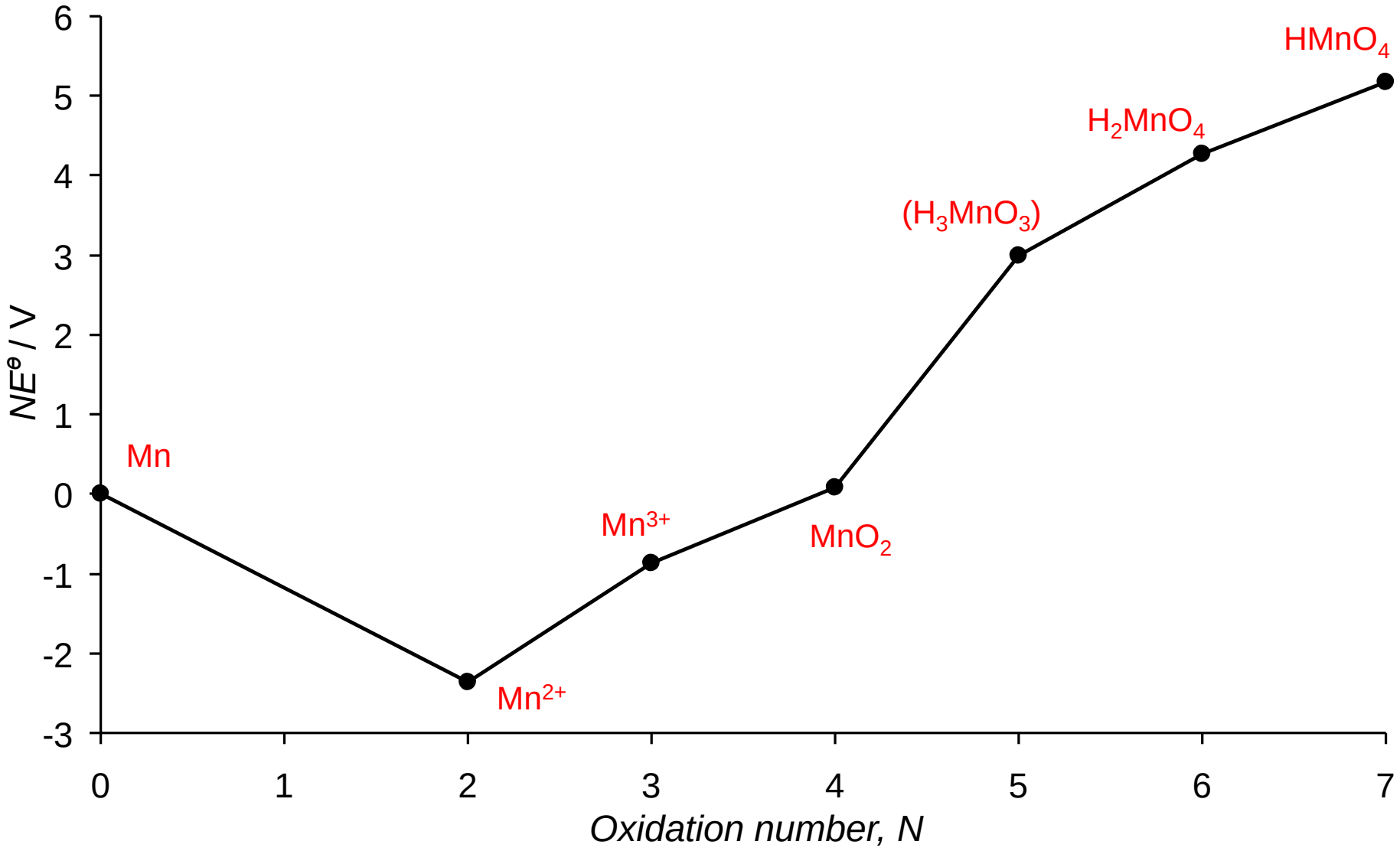




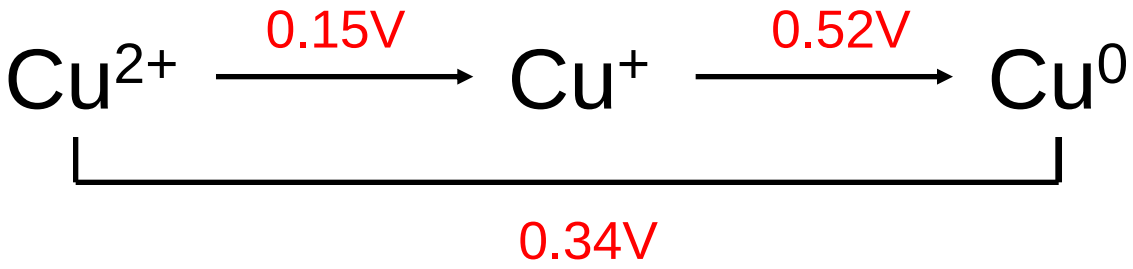




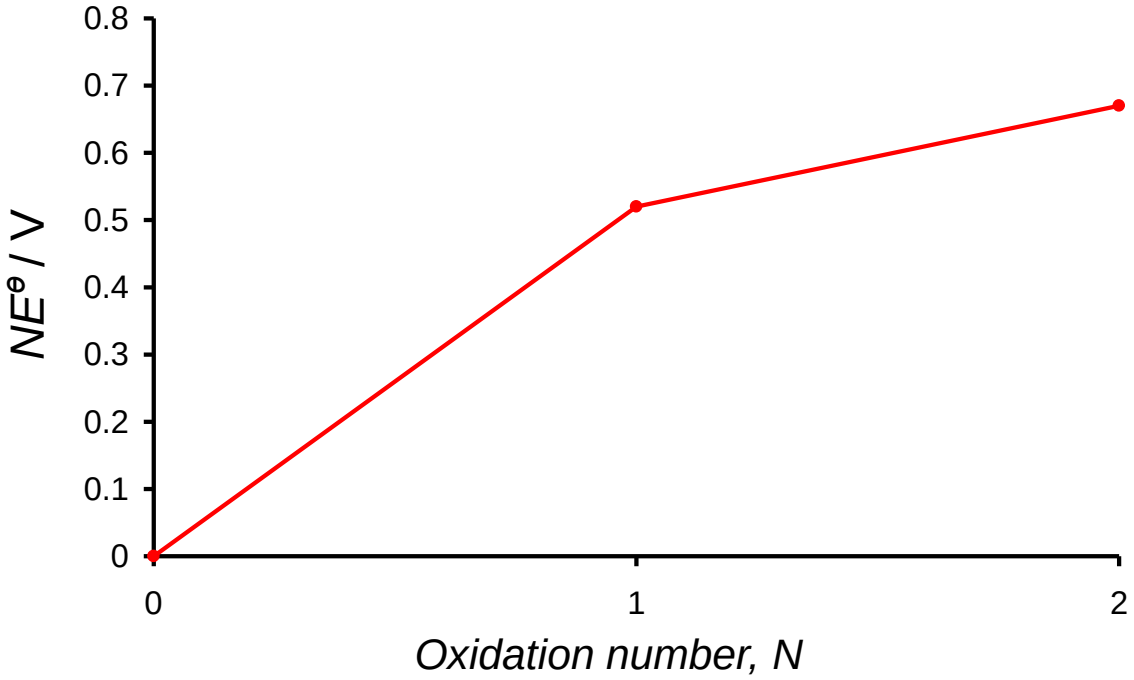
Frost diagram Manganese (acidic)

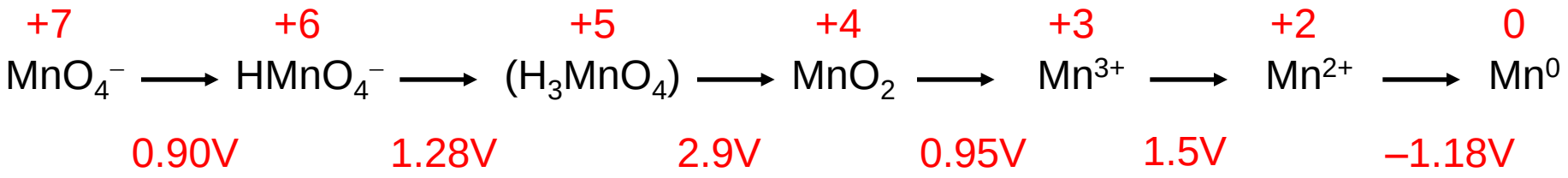


Latimer diagrams



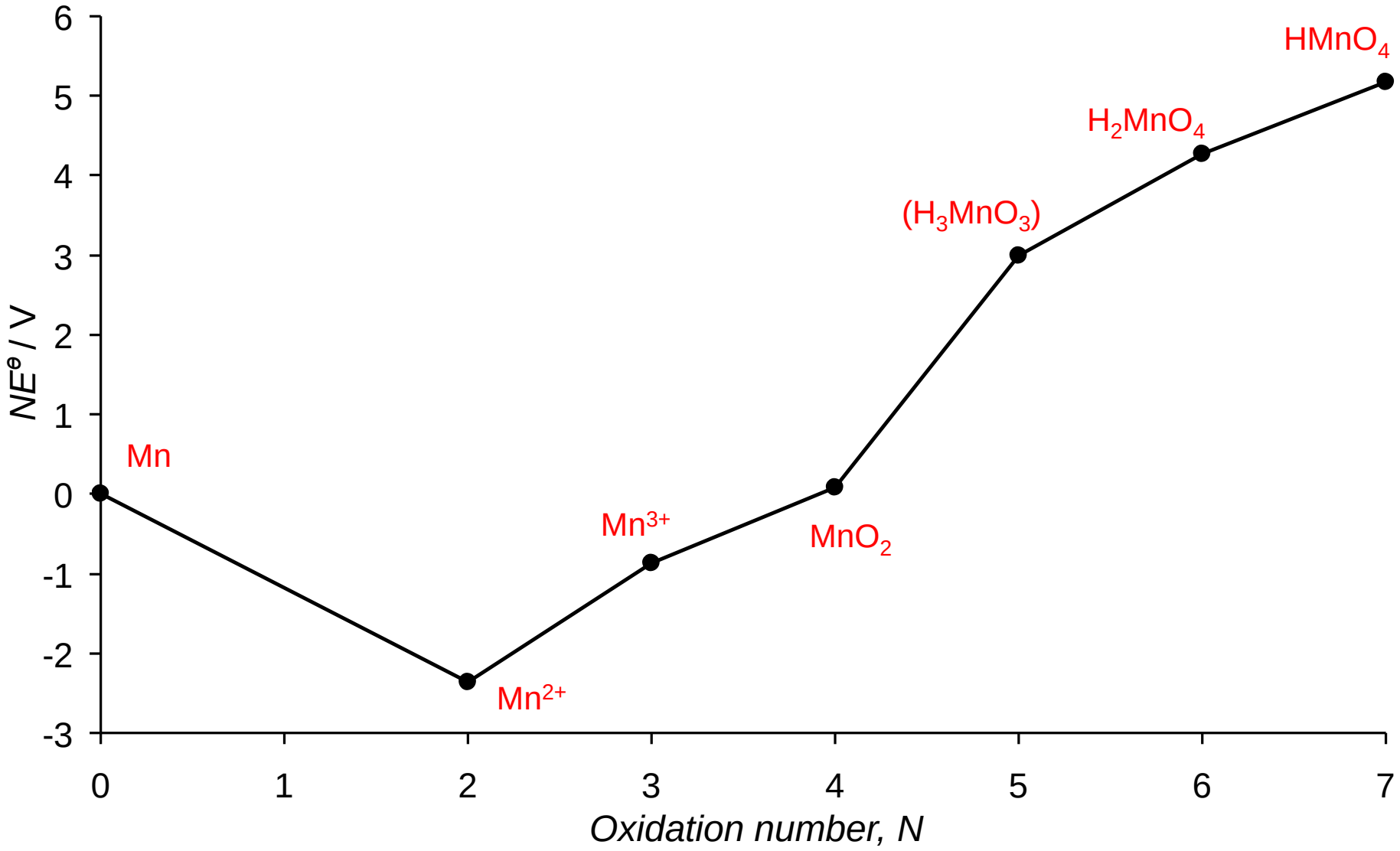
N	*N E⁰*
0	0
+1	0 + 0.52
+2	0.52 + 0.15





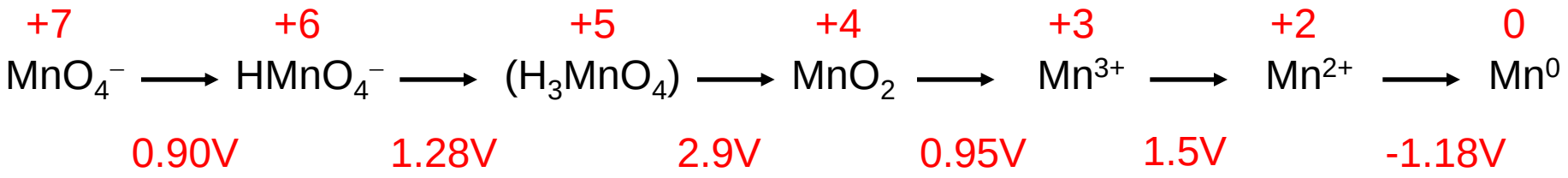
N	*Species*	*Calculation*	*nE°*
0	Mn	0	0.0
+2	Mn^{2+}	2 × –1.18	–2.36
+3	Mn^{3+}	1 × 1.5 + –2.36	–0.86
+4	MnO_2	1 × 0.95 + –0.86	0.09
+5	H_3MnO_4	1 × 2.9 + 0.09	2.99
+6	$HMnO_4^-$	1 × 1.28 + 2.99	4.27
+7	MnO_4^-	1 × 0.90 + 4.27	5.17

Frost diagram Manganese (acidic)



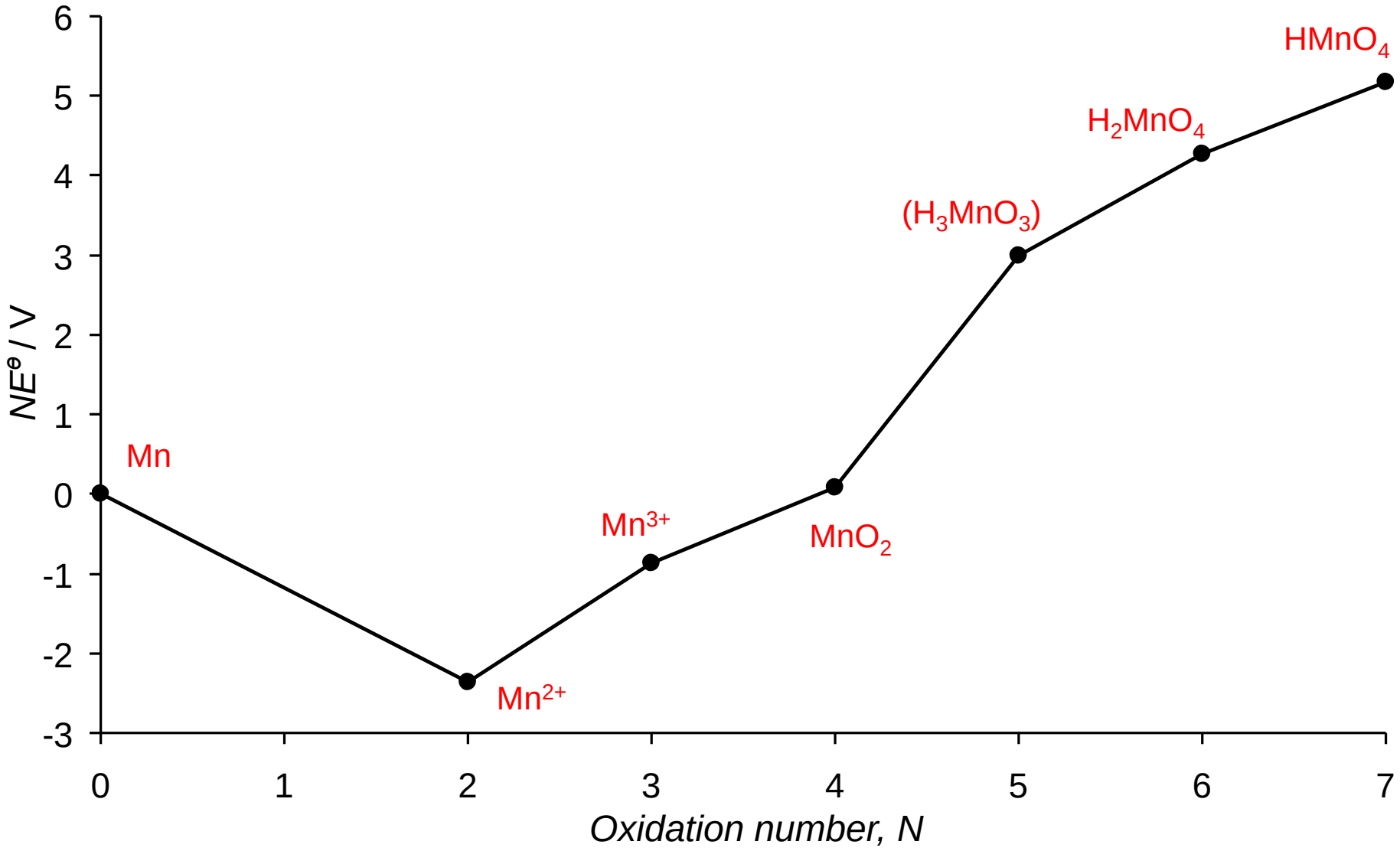
Acids, bases and solution equilibria

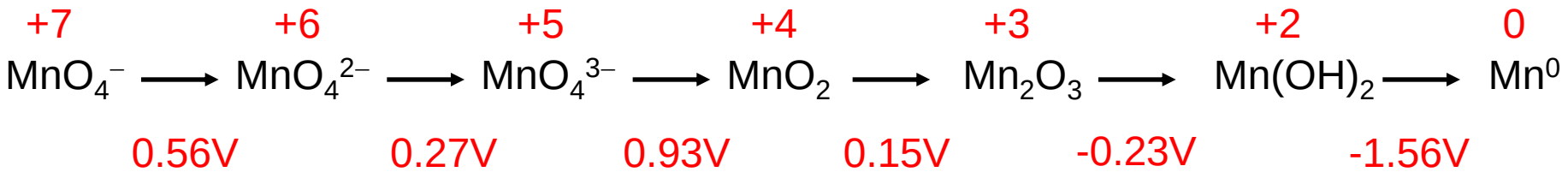
LECTURE 4



N	***Species***	***Calculation***	***nE^{e}***
0	Mn	0	0.0
+2	Mn^{2+}	2 × –1.18	–2.36
+3	Mn^{3+}	1 × 1.5 + –2.36	–0.86
+4	MnO_2	1 × 0.95 + –0.86	0.09
+5	H_3MnO_4	1 × 2.9 + 0.09	2.99
+6	$HMnO_4^-$	1 × 1.28 + 2.99	4.27
+7	MnO_4^-	1 × 0.90 + 4.27	5.17

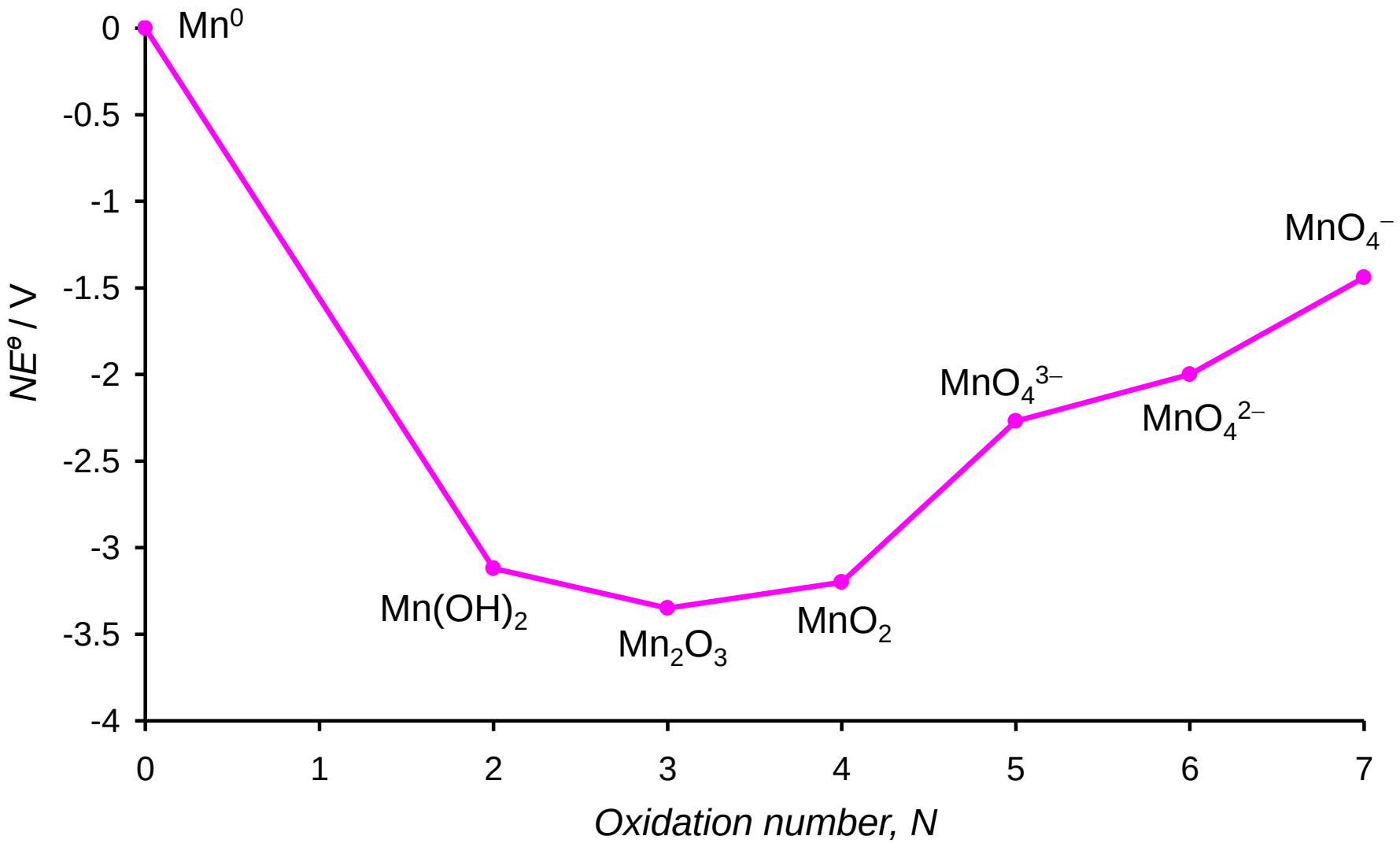
Frost diagram Manganese (acidic)



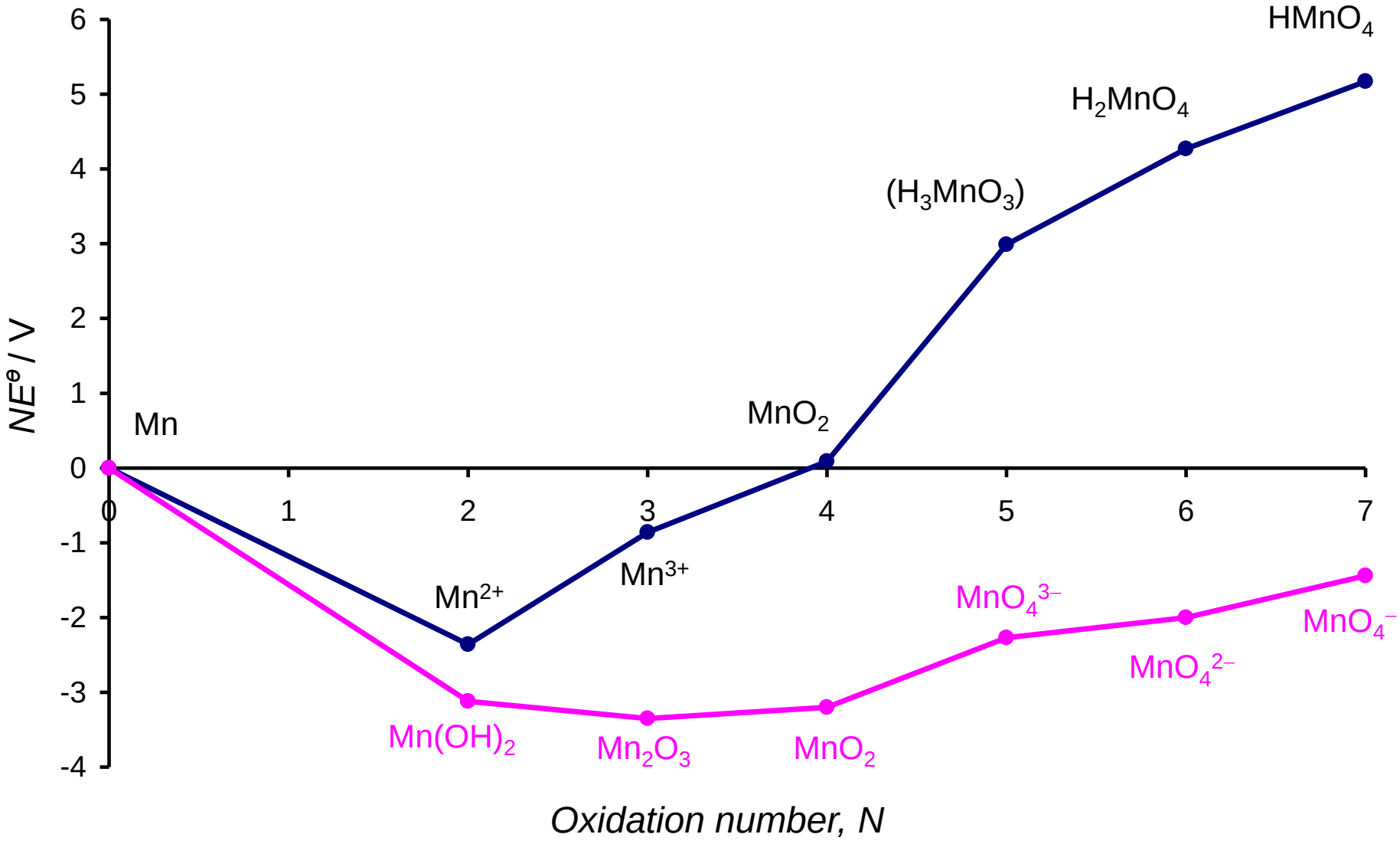


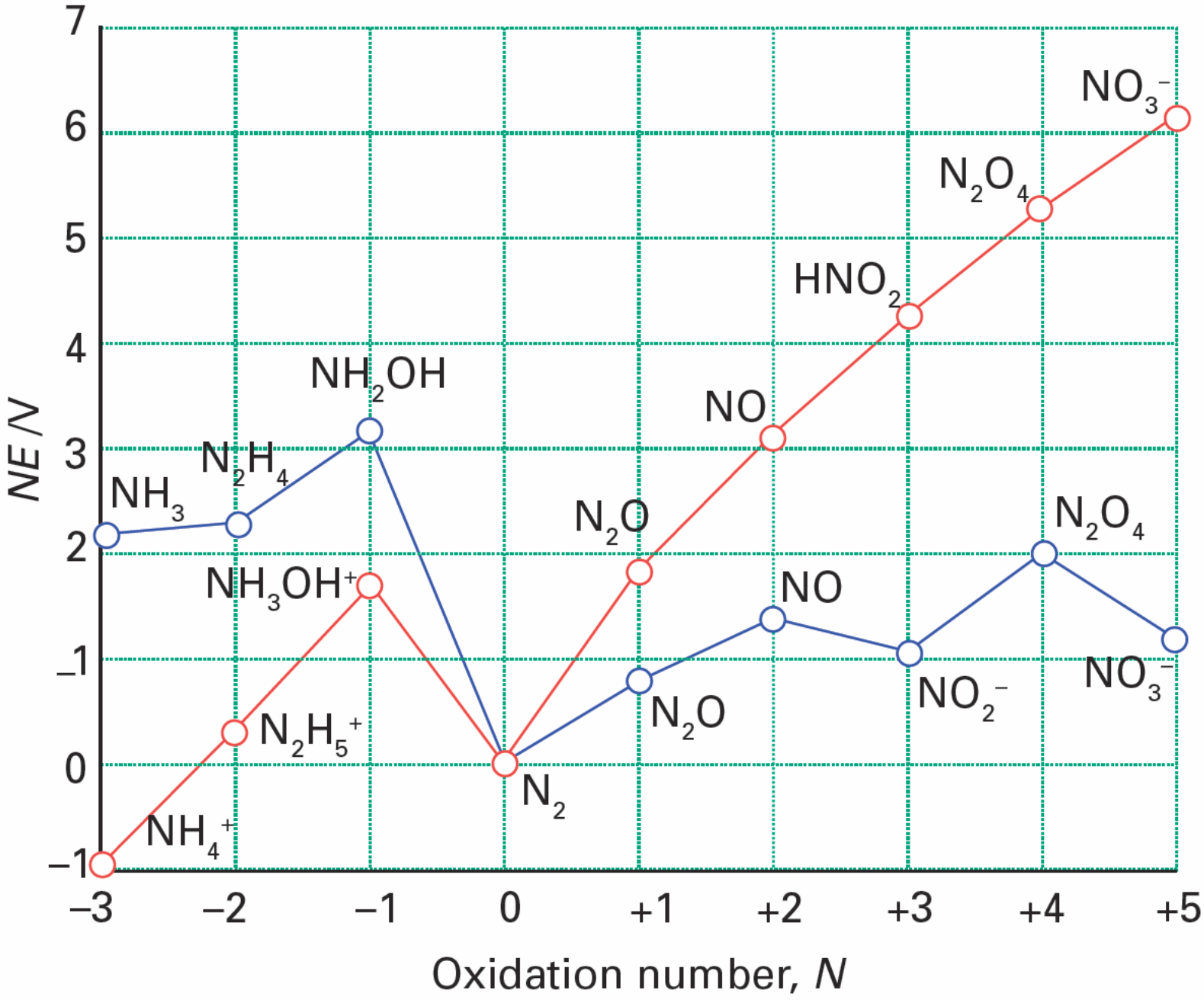
N	*Species*	*Calculation*	*nE°*
0	Mn	0	0.0
+2	Mn^{2+}	2 × –1.56	–3.12
+3	Mn^{3+}	1 × –0.23 + –3.12	–3.35
+4	MnO_2	1 × 0.15 + –3.35	–3.20
+5	H_3MnO_4	1 × 0.93 + –3.20	–2.27
+6	$HMnO_4^-$	1 × 0.27 + –2.27	–2.0
+7	MnO_4^-	1 × 0.56 + –2.0	–1.44

Frost diagram Manganese (basic)



Frost diagram Manganese




7
6
5
4
3
2
–1
0
–1
–3
–2
–1
0
+1
+2
+3
+4
+5
NE /V
Oxidation number, N
NH3
N2H4
NH2OH
NH3OH+
N2H5+
NH4+
N2
N2O
NO
HNO2
N2O4
NO3–
N2O
NO
NO2–
N2O4
NO3–

Stabilisation of oxidation states by complexation

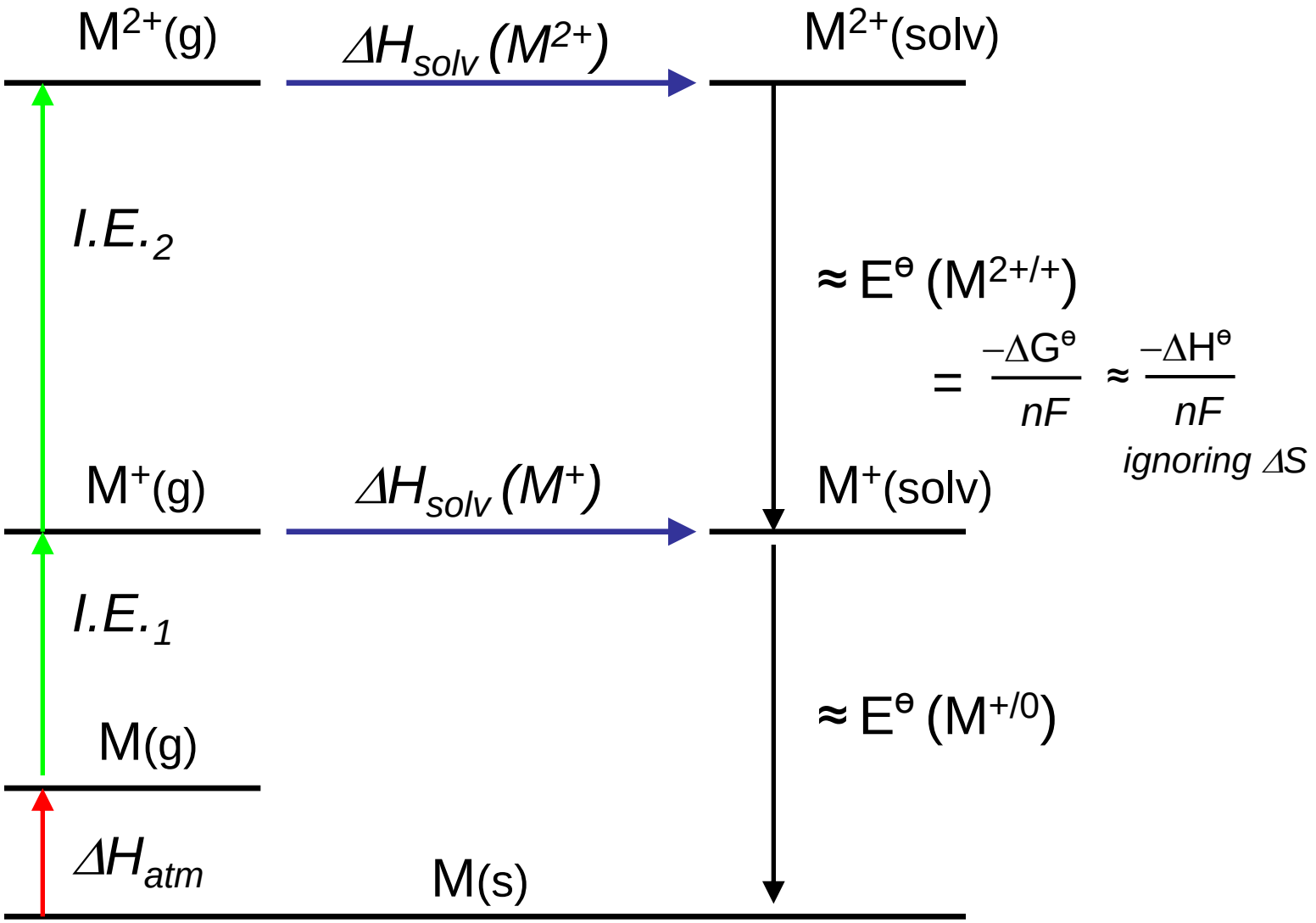
$$[Fe^{III}(CN)_6]^{3-} + e^- \rightleftharpoons [Fe^{II}(CN)_6]^{4-}$$

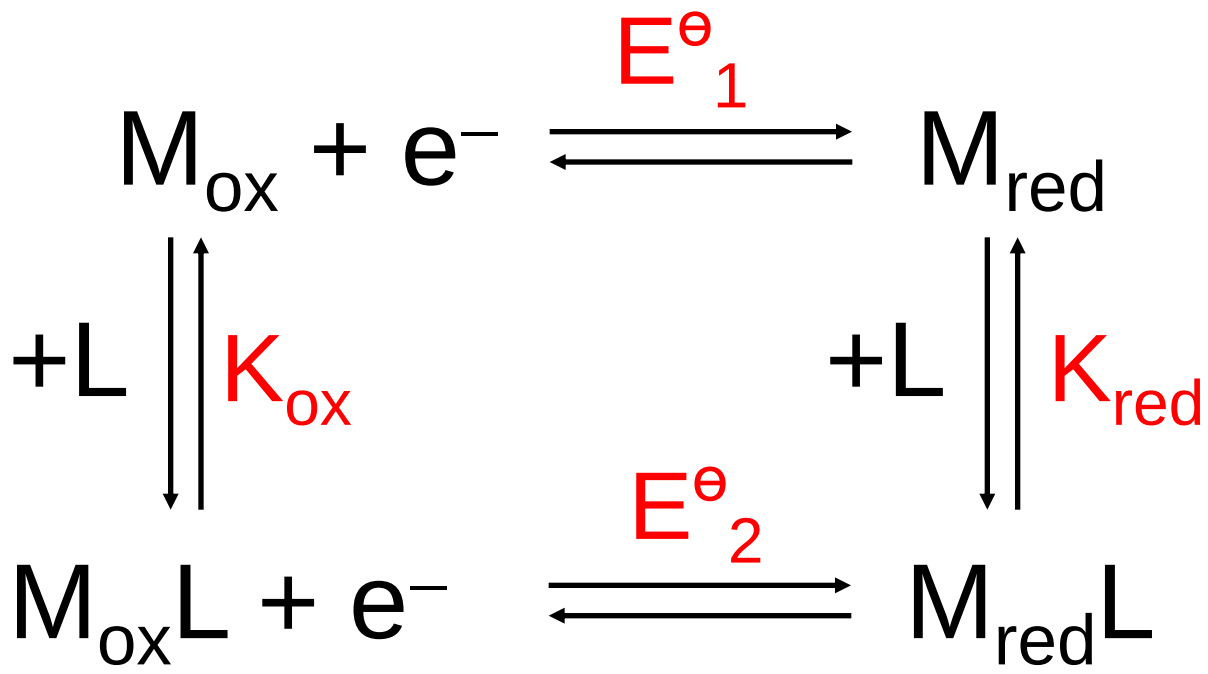
$$E^\ominus = 0.41V$$

However,

$$Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$$

$$E^\ominus = 0.77V$$

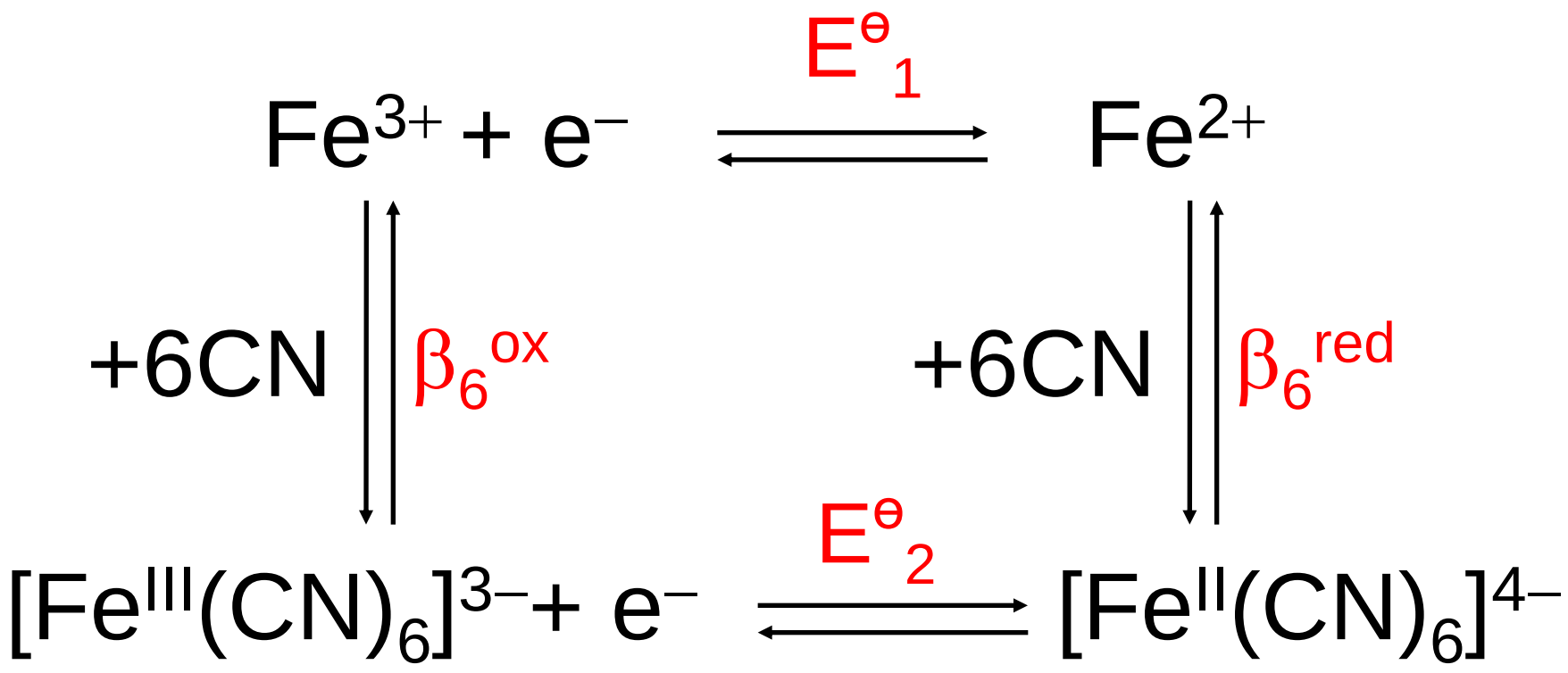

M2+(g)
ΔHsolv (M2+)
M2+(solv)
I.E.2
≈ Eθ (M2+/+)
= −ΔGθ / nF ≈ −ΔHθ / nF
ignoring ΔS
M+(g)
ΔHsolv (M+)
M+(solv)
I.E.1
≈ Eθ (M+/0)
M(g)
ΔHatm
M(s)



$$\Sigma \Delta G^{\ominus} = 0$$

$$-nE^{\ominus}_1 F - RT\ln K_{red} + nE^{\ominus}_2 F + RT\ln K_{ox} = 0$$

$$E^{\ominus}_2 - E^{\ominus}_1 = \frac{2.3RT}{n\,F} \log \frac{K_{red}}{K_{ox}}$$



$$E^o_2 - E^o_1 = (2.3RT/F)\log(\beta_6^{red}/\beta_6^{ox})$$

pH dependence of redox equilibria

Nernst equation

$$E = E^{\ominus} + \frac{2.3RT}{n\,F} \log \frac{[A_{ox}]}{[A_{red}]}$$

$$A_{ox} + 2H^+ + 2e^- \rightleftharpoons A_{red}H_2$$

$$E = E^\ominus + \frac{2.3RT}{2F} \log \frac{[A_{ox}][H^+]^2}{[A_{red}H_2]} =$$

$$= E^\ominus + \frac{2.3RT}{2F} \log \frac{[A_{ox}]}{[A_{red}H_2]} - 2 \times \frac{2.3RT}{2F} pH$$

$$= E^\ominus + \frac{2.3RT}{2F} \log \frac{[A_{ox}]}{[A_{red}H_2]} - \frac{2.3RT}{F} pH$$

pH independent **pH dependent**

$$= E^{\ominus} + \frac{0.059}{2} \log \frac{[A_{ox}]}{[A_{red}H_2]} - 0.059pH$$

In general, for reaction:

$$A_{ox} + mH^+ + ne^- \rightleftharpoons A_{red}H_m$$

$$= E^{\ominus} + \frac{0.059}{n} \log \frac{[A_{ox}]}{[A_{red}H_m]} - \frac{m}{n} 0.059pH$$

pH dependence

“Trimmed down” equation:

Assuming concentrations of A_{ox}, $A_{red}H_m$ are 1M (unit activities):

$$E_{pH} = E^{\ominus} - 0.059 \frac{m}{n} pH$$

Oxo-transfer reactions

$$ClO_4^- + 2e^- \rightleftharpoons ClO_3^- + \text{‘O’}$$

‘O’ = O^{2-}, a very strong base

write as:

$$ClO_4^- + 2H^+ + 2e^- \rightleftharpoons ClO_3^- + H_2O$$

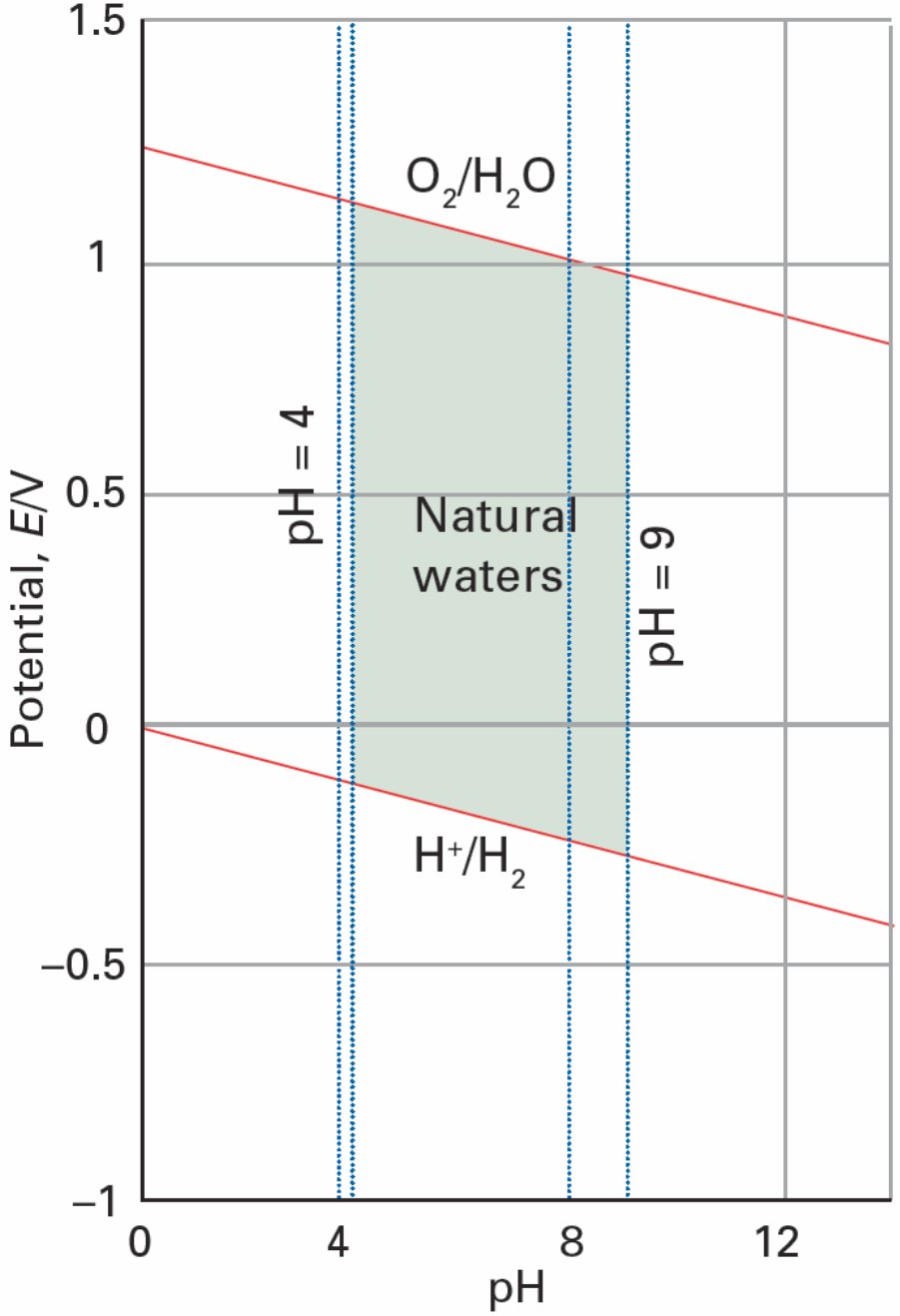
$\frac{m}{n} = 1$

pH dependence = –0.059 V/pHunit

Pourbaix diagrams

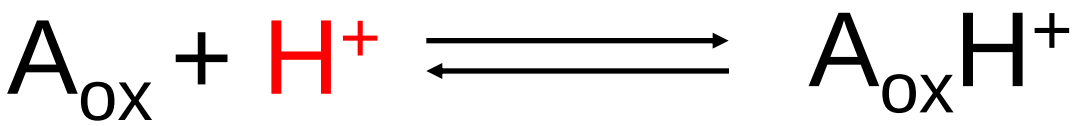
Show how E varies with pH

$$gradient = -0.059 \frac{m}{n}$$



Pourbaix diagrams

Include proton transfer within Nernst framework



m = 1, n=0 *gradient = ∞*

pH < pK$^{H}_{ox}$

$$A_{ox}H^{+} + e^{-} \rightleftharpoons A_{red}H$$

m = 0, n = 1 *gradient = 0*

---

pK$^{H}_{ox}$ < pH < pK$^{H}_{red}$

$$A_{ox} + H^{+} + e^{-} \rightleftharpoons A_{red}H$$

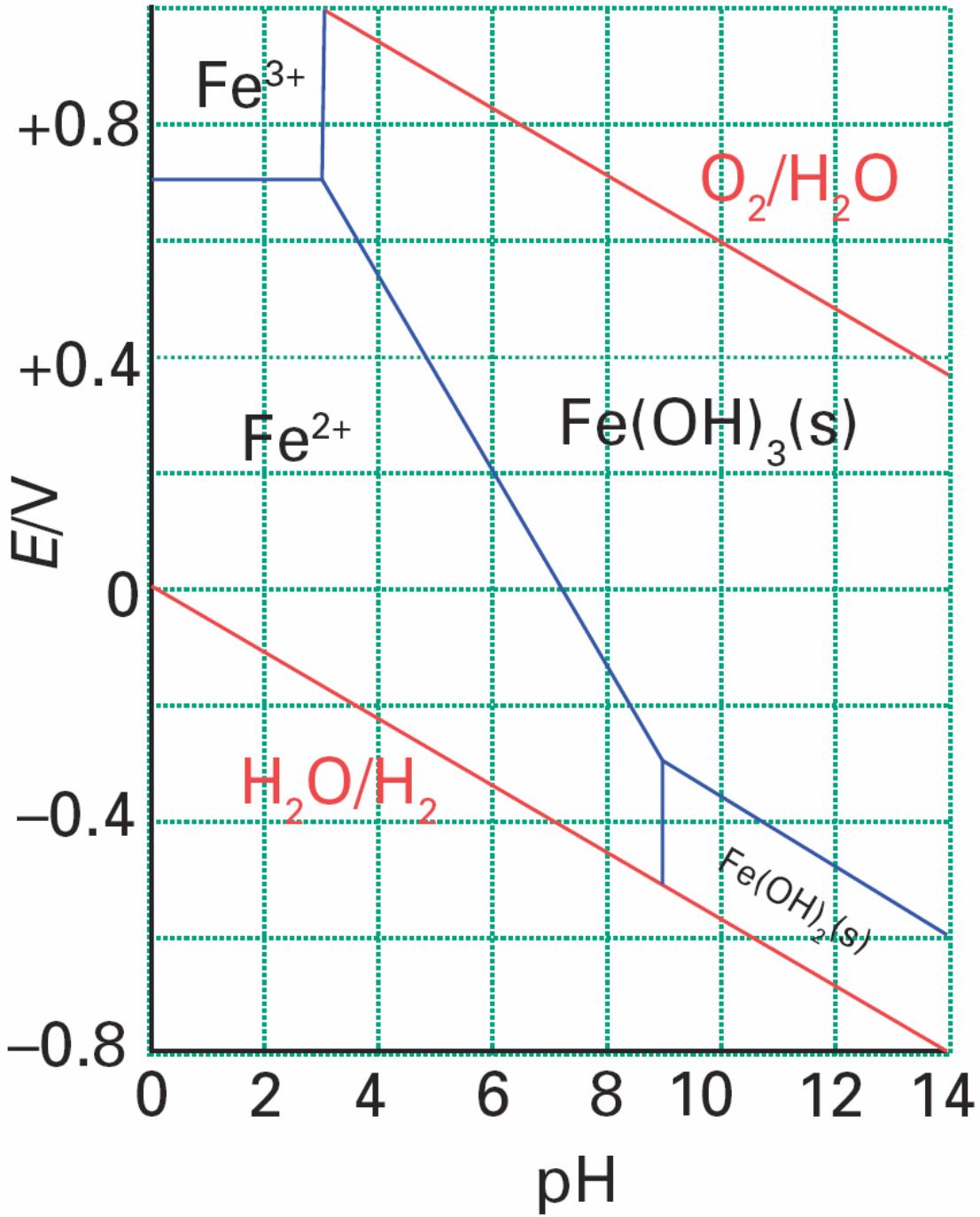
m = 1, n = 1 *gradient = –0.059*

---

pH > pK$^{H}_{red}$

$$A_{ox} + e^{-} \rightleftharpoons A_{red}^{-}$$

m = 0, n = 1 *gradient = 0*


Fe3+
+0.8
O2/H2O
+0.4
Fe2+
Fe(OH)3(s)
E/V
0
H2O/H2
–0.4
Fe(OH)2(s)
–0.8
0
2
4
6
8
10
12
14
pH

Constructing a Pourbaix diagram

1 $Fe^{3+}_{(aq)} + e^- \rightleftharpoons Fe^{2+}_{(aq)}$ $E^e = 0.77V$

m = 0, n = 1 *slope = 0*

---

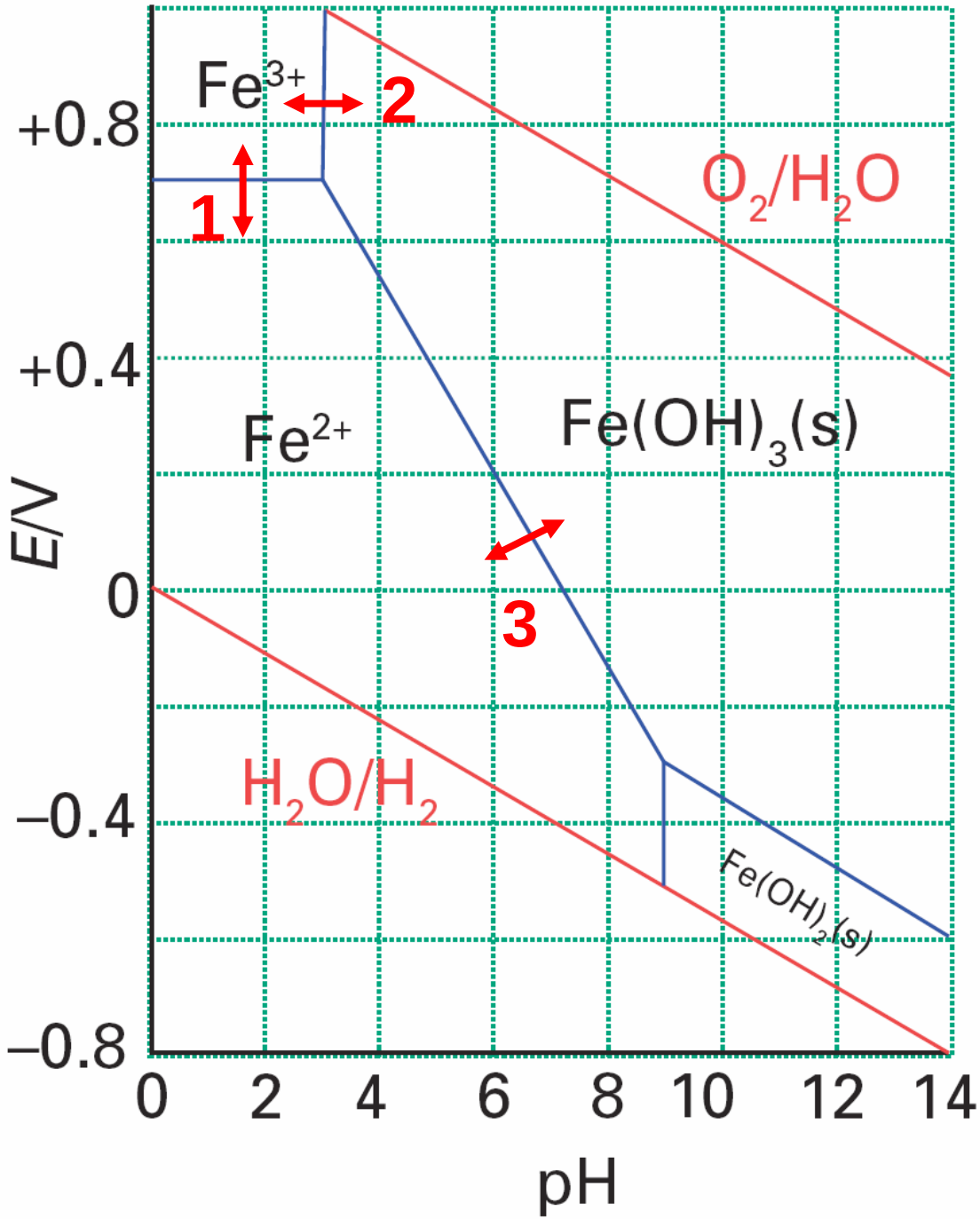
2 $Fe^{3+}_{(aq)} + 3H_2O \rightleftharpoons Fe(OH)_{3(s)} + 6H^+$

n = 0 *slope = ∞ (pK ≈ 3)*

---

3 $Fe(OH)_{3(s)} + 3H^+ + e^- \rightleftharpoons Fe^{2+}_{(aq)} + 3H_2O$

n = 1, m=3 *slope = –0.177*


Fe3+
2
1
O2/H2O
+0.8
+0.4
Fe2+
Fe(OH)3(s)
E/V
0
3
H2O/H2
–0.4
Fe(OH)2(s)
–0.8
0
2
4
6
8
10
12
14
pH

Constructing a Pourbaix diagram (continued)

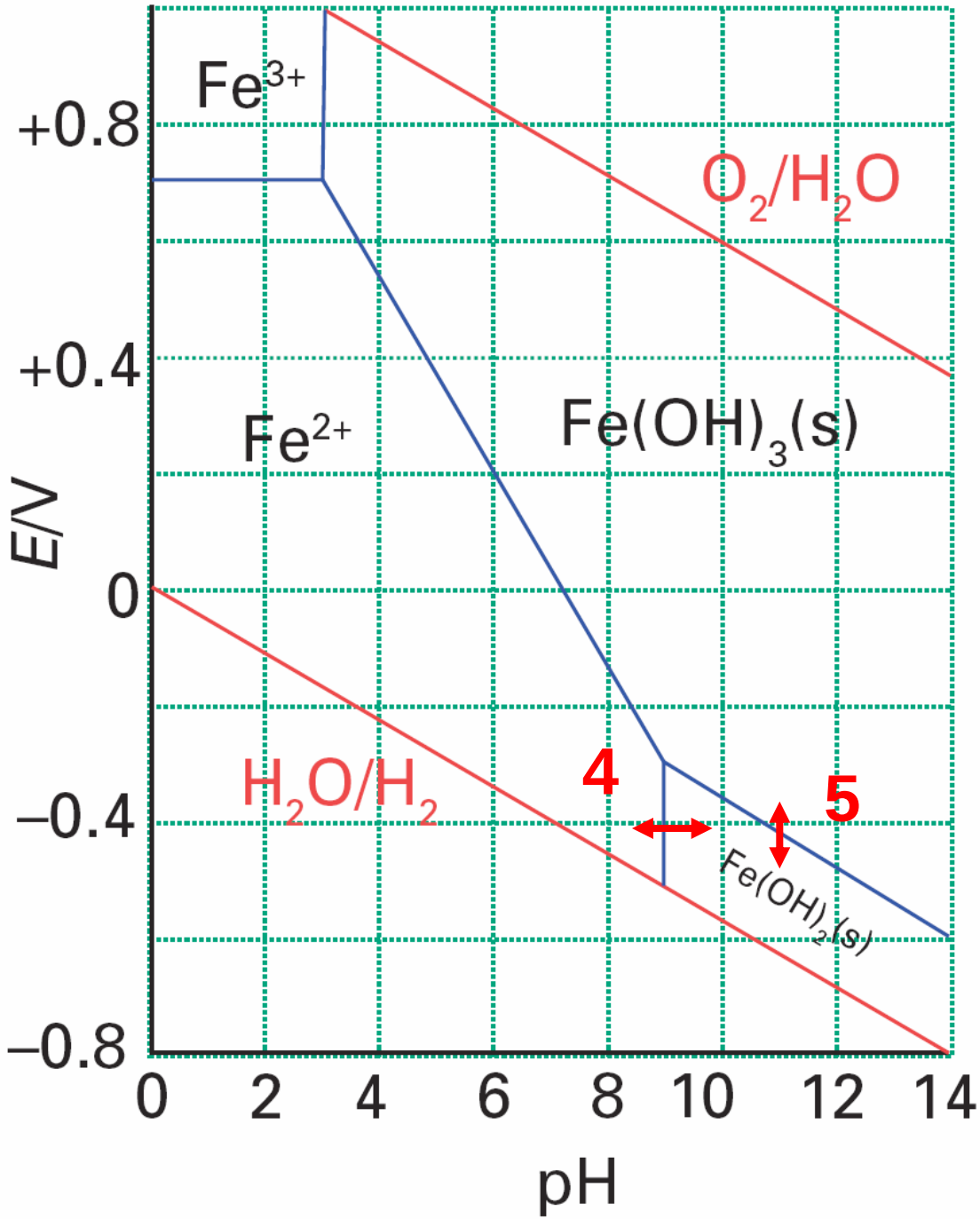
4 $Fe^{2+}_{(aq)} + 2H_2O \rightleftharpoons Fe(OH)_{2(s)} + 2H^+$

m = 0, n = 0 *slope = ∞ (pK ≈ 9)*

---

5 $Fe(OH)_{3(s)} + H^+ + e^- \rightleftharpoons Fe(OH)_{2(s)} + H_2O$

m = 1, n = 1 *slope = –0.059*


Fe3+
+0.8
O2/H2O
+0.4
Fe2+
Fe(OH)3(s)
E/V
0
H2O/H2
4
5
–0.4
Fe(OH)2(s)
–0.8
0
2
4
6
8
10
12
14
pH

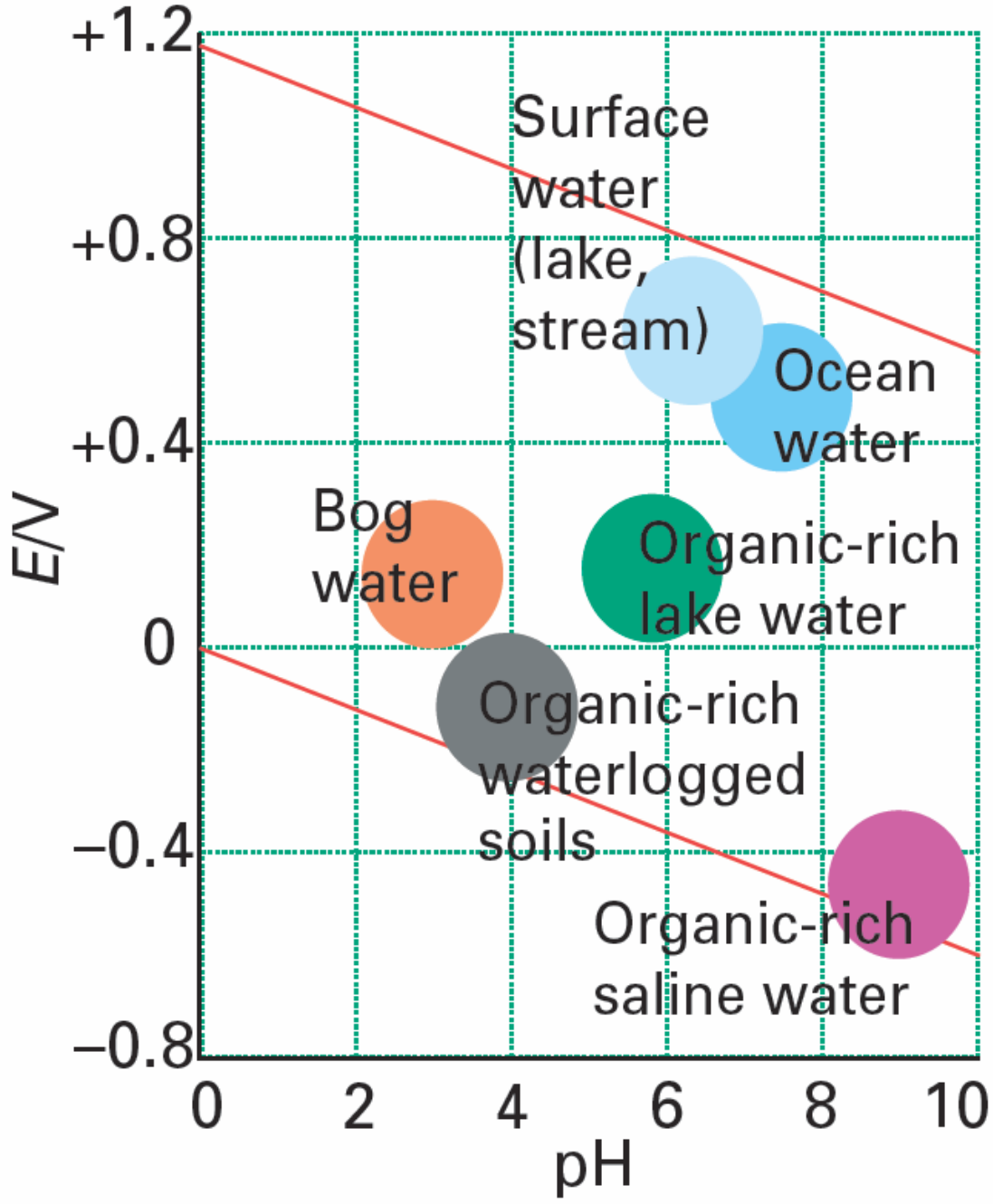
For water the limits are:

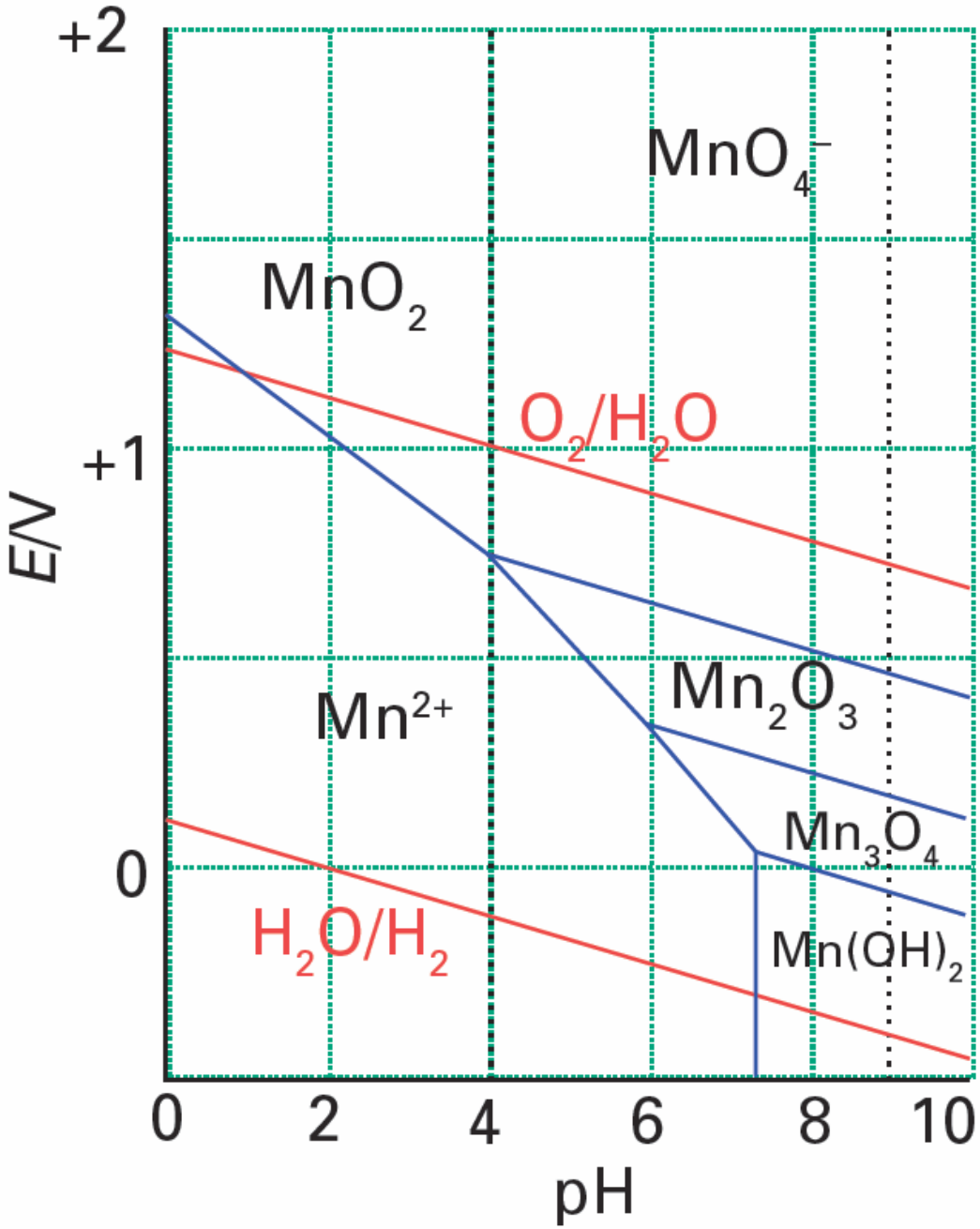
$$O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \qquad E^\ominus = 1.23V$$

m = 2, n = 2 *slope = –0.059*

$$2H^+_{aq} + 2e^- \rightleftharpoons H_2 \qquad E^\ominus = 0V$$

m = 2, n = 2 *slope = –0.059*


+1.2
+0.8
+0.4
0
–0.4
–0.8
E/V
0
2
4
6
8
10
pH
Surface water (lake, stream)
Ocean water
Bog water
Organic-rich lake water
Organic-rich waterlogged soils
Organic-rich saline water


+2
+1
0
E/V
MnO4−
MnO2
O2/H2O
Mn2+
Mn2O3
Mn3O4
Mn(OH)2
H2O/H2
0
2
4
6
8
10
pH