# Acid Rain: Non-metal oxides



# **Element oxides**

Various element oxides can combine with water to produce acids or bases

Basic oxides – upon reaction with water form materials that are stronger Brønsted bases than water (decrease [H<sup>+</sup>]).

Acidic oxides – upon reaction with water form materials that are stronger Brønsted acids than water (increase [H<sup>+</sup>])

Amphoteric oxides – upon reaction with water form materials that can react with both bases and acids

Examples:  $Li_2O$ , CaO, and BaO react with water to form basic solutions and can react with acids directly to form salts.

Likewise,  $SO_3$ ,  $SO_2$ ,  $CO_2$ ,  $N_2O_5$ ,  $P_2O_3$  and  $P_2O_5$  form acidic aqueous solutions and can react directly with bases to give salts.

Element oxides: Which react with water to give E<sup>+</sup>(OH)<sup>-</sup> and which give EO<sup>-</sup>H<sup>+</sup>

Basic oxides – typically metal oxides (oxides of the more **electropositive** elements:  $Na_2O$ , MgO, CaO, etc.)

Acidic oxides – typically non-metal oxides (oxides of the more **electronegative** elements)

## Amphoteric oxides – typically oxides of the elements of intermediate electronegativity

\*\*For the same element, the higher the oxidation state, the more acidic the oxide is.

<u>Amphoteric</u> is not to be confused with <u>amphiprotic</u> – a substance that can act as both a Brønsted acid and base



**Oxides as Acid and Basic Anhydrides** 

## Basic Oxides (usually "ionic")

CaO + 2  $H_2O$  —> Ca<sup>2+</sup> + 2 OH<sup>-</sup>, a moderately strong base

 $[O^{2-}] + H_2O \longrightarrow 2OH^-$  K > 10<sup>22</sup>

Alkali metal and alkaline earth oxides are basic (dissolve in acid). Or, they react directly with acidic oxides:

$$CaO + SO_3 \longrightarrow Ca^{2+} SO_4^{2-}$$
  
 $CaO + CO_2 \longrightarrow Ca^{2+} CO_3^{2-}$ 

### Examples of Acidic Oxides, or Acid Anhydrides, reactions with water give "oxy-acids"



Note: The non-metal element-oxygen (E–O) bond is not broken on dissolution.

#### either

an E – O – E group is hydrolyzed by water (as in  $P_4O_{10}$ );

#### or

water is added across the E=O double bond (as in  $CO_2$ ).

### Examples of Acidic Oxides, or Acid Anhydrides, reactions with water give "oxy-acids"



Acidic Oxides (Non-metal Oxides or Acid Anhydrides)

element-oxygen (E–O) bond is not broken on dissolution either

an E – O – E group is hydrolyzed by water

### or

water is added across a double bond

Acidic Oxides not soluble in water will dissolve in basic aqueous solutions to produce salts
 eg. As<sub>2</sub>O<sub>3</sub> + 2NaOH(aq) ---> 2NaH<sub>2</sub>As O<sub>3</sub>
 (Often seen for anhydrides of weaker acids.)

# **Amphoteric Oxides**

Dissolve in acids or bases - if strong enough.

Eg., BeO, SnO, certain forms of  $Al_2O_3$ 

In strong <u>acids</u>:

 $ZnO + 4 HCl(aq) \longrightarrow H_3O^+ [ZnCl_4]^{2-}$ 

 $ZnO + 2HNO_{3}(aq) \longrightarrow Zn(OH_{2})_{6}^{2+} + NO_{3}^{-}$ 

In strong <u>base</u>:  $ZnO + 2NaOH(aq) \longrightarrow 2Na^{+}(aq) + [Zn(OH_4)]^{2-}(aq)$ 

#### Transition Metal Oxides Acidity or Basicity Depends on Oxidation Number (State)



MnO is basic; MnO<sub>2</sub> is amphoteric MnO<sub>3</sub> is acidic

Figure 4.6 Shriver, et al.

# Acidity constants

Acidity constants define the "strength" of an acid or its propensity to dissociate (which is a propensity to donate proton to the solvent)

For dilute solutions of acid HA,

```
K_a = [H^+][A^-] / [HA]
```

 $pK_a = -log K_a$ 

K<sub>a</sub> is a constant at a given T for a given solvent; it is an intrinsic property of a compound

Some empirical observations:



# Pauling's rules, #1 and #2, for pKa values: #1. The pKa of an acid (O)<sub>p</sub>E(OH)<sub>q</sub> is pKa = 8 - 5p

#2. Generally, successive pKa's increase by 5 per ionization (i.e. for loss of the second, third proton etc.); increase in pKa means <u>decrease</u> in K<sub>a</sub>.



 $\Delta G^{0} = -RT \ln K_{eq}$  $\Delta G^{0} = \Delta H^{0} - T\Delta S^{0}$ 



# What determines aqueous acid "strength"?

More O attached to central atom => Polarization of the O-H bond in oxyacids making it "easier" to break?

Acid strengths:	$HCIO_4 > HCIO_3 > HCIO_2 > HCIO_2$
By Pauling's rules:	Expt'l
$HCIO_4 pK_a = 8 - 5x3 = -7$	-10
$HClO_3 pK_a = 8 - 5x2 = -2$	- 1
$HCIO_2 pK_a = 8 - 5x1 = 3$	2
HClO $pK_a = 8 - 5x0 = 8$	7.5
ic it	

Or is it

Stabilization of the anion by delocalization of the anionic charge?

## **Thermodynamics:** $\Delta G^0 = -RT \ln K_{eq}$

How are negative pKa's measured?

evans.rc.fas.harvard.edu/pdf/evans\_pKa\_table.pdf

# Thermodynamics and pK<sub>a</sub>



#### Lists and more lists: David Evans, Harvard, and Bordwell, Wisconsin

_	Substrate	pKa	H <sub>2</sub> O	(DMSO)	Substrate	рКа	H <sub>2</sub> O(DMSO)	Substrate	pKa	H <sub>2</sub> O	(DMSO)	Substrate	pKa	H <sub>2</sub> O	(DMSO)
	INORG		ACIDS	;	CARB	OXYLIC	ACIDS	ALC	соно	LS		PROTON	ATED \$	SPECI	ES
	H <sub>2</sub> O		15.7	(32)	Ŷ			НОН		15.7	(31.2)	0			
	H₃O⁺		-1.7		х			MeOH		15.5	(27.9)	Ph Nt OH		-12.4	
	H <sub>2</sub> S		7.00		X= CH <sub>3</sub>	_	4.76 (12.3) 1.68	<i>i</i> -PrOH		16.5	(29.3)	тон Ц		-78	
	HBr		-9.00	(0.9)	CH <sub>2</sub> RO	2	2.66	t-BuOH		17.0	(29.4)	Ph OH		1.0	
	HCI		-8.0	(1.8)	CH <sub>2</sub> CI		2.86	<i>c</i> -hex₃COH		24.0		<sup>•</sup> OH ∐		-62	
	HF		3.17	(15)	CH <sub>2</sub> Br		2.86	CF <sub>3</sub> CH <sub>2</sub> OH		12.5	(23.5)	Ph CH <sub>3</sub>			
			75	) í	CH <sub>2</sub> I		3.12	(CF <sub>3</sub> ) <sub>2</sub> CHOH		9.3	(18.2)	н 1.		65	
			10				0.65	C <sub>6</sub> H <sub>5</sub> OH		9.95	(18.0)	Ph <sup>O+</sup> Me		-0.5	
			-10		CF3		-0.25	m-O2NC6H4	ЮH	8.4		H		2.0	
	HCN		9.4	(12.9)	Н		3.77	p-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	OH	7.1	(10.8)	Me		-0.0	
	HN <sub>3</sub>		4.72	(7.9)	HO		3.6, 10.3	p-OMeC <sub>6</sub> H <sub>4</sub> C	ЭН	10.2	(19.1)			-2 05	
	HSCN		4.00		C <sub>6</sub> H <sub>5</sub>	п	4.2 (11.1)	2-napthol			(17.1)	Ч		2.00	
	H <sub>2</sub> SO <sub>3</sub>		1.9, 7	7.21	m-O_N(	6⊓4 Ъ.Н.	2.17	OXIMES & HY	(DRO)		ACIDS	Me <sup>O+</sup> H		-2.2	
	H-90.		-30 1	1 99	p-02NC	26 <sup>1</sup> 14 C <sub>6</sub> H₄	3.44	N_OH				tOH Į		-1.8	
	12004		0.0, 1		 <i>o</i> -CIC <sub>6</sub> ⊦	4 14	2.94	<u>ľ</u>		11.3	(20.1)	Me			
	H <sub>3</sub> PO₄		2.12, 12.32	7.21,	m-CIC <sub>6</sub>	H <sub>4</sub>	3.83	Ph Ph						0.70	
	HNO <sub>3</sub>		-1.3		p-CIC <sub>6</sub> H	H <sub>4</sub>	3.99			8.88 (NH)	(13.7)	N+-OH		0.79	(+1.63)
	HNO <sub>2</sub>		3.29		o-(CH3)	<sub>3</sub> N⁺C <sub>6</sub> H <sub>4</sub>	1.37	· по й		(111)		⊕l			
	H₂CrO₄		-0.98,	6.50	<i>р</i> -(СН <sub>3</sub> )	<sub>3</sub> N⁺C <sub>6</sub> H	4 <mark>3.43</mark>	Ph N <sup>OH</sup>			(18.5)	Me—N—OH I Me			(+5.55)
	CH <sub>3</sub> SO <sub>3</sub> H		-2.6	(1.6)	p-OMe0	C <sub>6</sub> H <sub>4</sub>	4.47	Me				SUL FINIC &	SULF	ONIC	
	CF <sub>3</sub> SO <sub>3</sub> H		-14	(0.3)	~ Î			PEF	ROXID	ES					
	NH <sub>2</sub> CI		9.24	` '	R	OH						o o		-2.6	
			0.22		R= H		4.25	MeOOH		11.5		Me			
			3.20		trans-C	D <sub>2</sub> H	3.02, 4.38	CH <sub>3</sub> CO <sub>3</sub> H		8.2				2.1	
	HOOH		0.11		cis-CO <sub>2</sub>	н	1.92, 6.23					Ph C OH			

pKa's of Inorganic and Oxo-Acids

Chem 206

\*Values <0 for  $H_2O$  and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods.

For a comprehensive compilation of Bordwell pKa data see: http://www.chem.wisc.edu/areas/reich/pkatable/index.htm

D.H. Ripin, D.A. Evans

#### pKa's of Nitrogen Acids



For a comprehensive compilation of Bordwell pKa data see: http://www.chem.wisc.edu/areas/reich/pkatable/index.htm pKa Table.2 11/4/05 1:43 PM

D.H. Ripin, D.A. Evans pKa's of CH bonds in Hydrocarbons and Carbonyl Compounds

Chem 2



\*Values <0 for H<sub>2</sub>O and DMSO, and values >14 for water and >35 for DMSO were extrapolated using various methods. For a comprehensive compilation of Bordwell pKa data see: http://www.chem.wisc.edu/areas/reich/pkatable/index.htm

pKa = 8 - 5(n)

Acidity Constants at	25°C*	
Acid	K <sub>a</sub>	pK <sub>a</sub>
trichloroacetic acid, CCl <sub>3</sub> COOH	$3.0  imes 10^{-1}$	0.52
benzene sulfonic acid, $C_6H_5SO_3H$	$2.0  imes 10^{-1}$	0.70
iodic acid, HIO <sub>3</sub>	$1.7  imes 10^{-1}$	0.77
sulfurous acid, $H_2SO_3$	$1.5 \times 10^{-2}$	1.81
chlorous acid, $HClO_2$	$1.0  imes 10^{-2}$	2.00
phosphoric acid, $H_3 \overline{PO}_4$	$7.6  imes 10^{-3}$	2.12
chloroacetic acid, CH <sub>2</sub> ClCOOH	$1.4 \times 10^{-3}$	2.85
lactic acid, CH <sub>3</sub> CH(OH)COOH	$8.4  imes 10^{-4}$	3.08
nitrous acid, $HNO_2$	$4.3 \times 10^{-4}$	3.37
hydrofluoric acid, HF	$3.5 \times 10^{-4}$	3.45

\*The values for  $K_a$  listed here have been calculated from  $pK_a$  values with more significant figures than shown so as to minimize rounding errors. Values for polyprotic acids—those capable of donating more than one proton—refer to the first deprotonation.

<sup>†</sup>The proton transfer equilibrium is  $B(OH)_3(aq) + 2 H_2O(l) \rightleftharpoons H_3O^+(aq) + B(OH)_4^-(aq)$ .

# Acidity and Structure

## *How does structure affect acidity of HA?*

1) Which element is the hydrogen bound to?

The acidity increases from left to right in the periodic table and from up to down (for main group elements). This is not the same trend as for electronegativities!

```
Thus HF > H_2O > NH_3 > CH_4,
```

```
but HI > HBr > HCl > HF, or H_2Te > H_2Se > H_2S > H_2O
```

For otherwise analogous compounds, the one with the heaviest element bound to H is the more acidic one. E.g.,  $CH_3SH$  is more acidic than  $CH_3OH$ ,  $PH_3$  is more acidic than  $NH_3$  etc.

### => H-A bond energies rule here.

2) Substituents on the atom that is directly bound to H in HA that stabilize the anion A<sup>-</sup> increase the acidity of HA. Generally, these are electron withdrawing substituents, however, both inductive and resonance effects must be taken into account .

## => Stability of Anion or conjugate base rules here.

Acidity Constants	s at 25°C*	
Acid	K <sub>a</sub>	pK <sub>a</sub>
formic acid, HCOOH	$1.8 imes10^{-4}$	3.75
benzoic acid, C <sub>6</sub> H <sub>5</sub> COOH	$6.5 \times 10^{-5}$	4.19
acetic acid, CH <sub>3</sub> COOH	$1.8 \times 10^{-5}$	4.75
carbonic acid, $H_2CO_3$	$4.3 \times 10^{-7}$	6.37
hypochlorous acid, HClO	$3.0 \times 10^{-8}$	7.53
hypobromous acid, HBrO	$2.0 \times 10^{-9}$	8.69
$\blacktriangleright$ boric acid, B(OH) <sub>3</sub> <sup>†</sup>	$7.2  imes 10^{-10}$	9.14
hydrocyanic acid, HCN	$4.9  imes 10^{-10}$	9.31
phenol, C <sub>6</sub> H <sub>5</sub> OH	$1.3  imes 10^{-10}$	9.89
hypoiodous acid, HIO	$2.3 \times 10^{-11}$	10.64

\*The values for  $K_a$  listed here have been calculated from  $pK_a$  values with more significant figures than shown so as to minimize rounding errors. Values for polyprotic acids—those capable of donating more than one proton—refer to the first deprotonation. <sup>†</sup>The proton transfer equilibrium is  $B(OH)_3(aq) + 2 H_2O(l) \rightleftharpoons$  $H_3O^+(aq) + B(OH)_4^-(aq)$ .

Acid name	Acid formula	Base formula	Base name
Strong acid			Very weak base
hydroiodic acid	HI	$I^-$	iodide ion
perchloric acid	HClO <sub>4</sub>	$ClO_4^-$	perchlorate ion
hydrobromic acid	HBr	Br <sup>-</sup>	bromide ion
hydrochloric acid	HCl	Cl-	chloride ion
sulfuric acid	$H_2SO_4$	$HSO_4^-$	hydrogen sulfate ion
chloric acid	HClO <sub>3</sub>	ClO <sub>3</sub> <sup>-</sup>	chlorate ion
nitric acid	HNO <sub>3</sub>	$NO_3^{-}$	nitrate ion
hydronium ion	$H_3O^+$	H <sub>2</sub> O	water
hydrogen sulfate ion	HŠO <sub>4</sub> <sup>-</sup>	$SO_4^{2-}$	sulfate ion
hydrofluoric acid	HF	$F^{-}$	fluoride ion
nitrous acid	HNO <sub>2</sub>	$NO_2^-$	nitrite ion
acetic acid	CH <sub>3</sub> COOH	CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup>	acetate ion
carbonic acid	$H_2CO_3$	HCO <sub>3</sub> <sup>-</sup>	hydrogen carbonate ion
hydrosulfuric acid	H <sub>2</sub> S	$HS^{-}$	hydrogen sulfide ion
ammonium ion	$NH_4^+$	NH <sub>3</sub>	ammonia
hydrocyanic acid	HCN	$CN^{-}$	cyanide ion
hydrogen carbonate ion	$HCO_3^-$	$CO_{3}^{2-}$	carbonate ion
methylammonium ion	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	$CH_3NH_2$	methylamine
water	H <sub>2</sub> O	OH-	hydroxide ion
ammonia	$N\bar{H}_3$	$\rm NH_2^-$	amide ion
hydrogen	H <sub>2</sub>	$H^{-}$	hydride ion
methane	$C\overline{H}_4$	$CH_3^{-}$	methide ion
hydroxide ion	OH-	$O^{2-}$	oxide ion
Very weak acid			Strong base

#### Conjugate Acid-Base Pairs Arranged by Strength

# Basicity constants

Basicity constants define the "strength" of a base or its propensity to dissociate or accept protons (e.g., from water)

For dilute aqueous solutions of base B,

```
K_{b} = [HB^{+}][OH^{-}] / [B]
```

 $pK_b = -logK_b$ 

 $K_b$  is a constant at a given T for a given solvent; it is an intrinsic property of a compound

Basicity Const	tants at 25°C*	
Base	$K_{ m b}$	pK <sub>b</sub>
urea, $CO(NH_2)_2$	$1.3 \times 10^{-14}$	13.90
aniline, $C_6H_5NH_2$	$4.3 \times 10^{-10}$	9.37
pyridine, $\tilde{C}_5 \tilde{H}_5 N^{-1}$	$1.8 \times 10^{-9}$	8.75
hydroxylamine, NH <sub>2</sub> OH	$1.1 \times 10^{-8}$	7.97
nicotine, $C_{10}H_{14}N_2$	$1.0 \times 10^{-6}$	5.98
morphine, $\tilde{C}_{17}H_{19}O_3N$	$1.6 \times 10^{-6}$	5.79
hydrazine, $NH_2NH_2$	$1.7  imes 10^{-6}$	5.77

\*The values for  $K_b$  listed here have been calculated from  $pK_b$  values with more significant figures than shown so as to minimize rounding

### Conjugate acid-base pairs Increasing strength of acid

The stronger the acid, the weaker its conjugate base

The weaker the acid, the stronger its conjugate base

 $K_a \times K_b = K_w$ 

The pK<sub>a</sub> value defines both acidity of the acid and the basicity of the conjugate base



Increasing strength of base

# Water

Water undergoes rapid autodissociation or autoprotolysis:

$$2H_2O \implies H_3O^+ + OH$$

The equilibrium constant at 25  $^{\circ}$ C for this process is K<sub>w</sub> = 1.0 × 10<sup>-14</sup>

Levelling Effect of water on strong acids: 100% ionized:  $HClO_4$   $H_2SO_4$  HCl HBr HBr HI $HNO_3$ 

# Basicity constants

Basicity constants define the "strength" of a base or its propensity to dissociate or accept protons (e.g., from water)

For dilute aqueous solutions of base B,

```
K_{b} = [HB^{+}][OH^{-}] / [B]
```

 $pK_b = -logK_b$ 

 $K_b$  is a constant at a given T for a given solvent; it is an intrinsic property of a compound

Basicity Const	tants at 25°C*	
Base	$K_{ m b}$	pK <sub>b</sub>
urea, $CO(NH_2)_2$	$1.3 \times 10^{-14}$	13.90
aniline, $C_6H_5NH_2$	$4.3 \times 10^{-10}$	9.37
pyridine, $\tilde{C}_5 \tilde{H}_5 N^{-1}$	$1.8 \times 10^{-9}$	8.75
hydroxylamine, NH <sub>2</sub> OH	$1.1 \times 10^{-8}$	7.97
nicotine, $C_{10}H_{14}N_2$	$1.0 \times 10^{-6}$	5.98
morphine, $\tilde{C}_{17}H_{19}O_3N$	$1.6 \times 10^{-6}$	5.79
hydrazine, $NH_2NH_2$	$1.7  imes 10^{-6}$	5.77

\*The values for  $K_b$  listed here have been calculated from  $pK_b$  values with more significant figures than shown so as to minimize rounding

Don't forget aqua acids!!!

Other topics within oxo acids and bases: Polyoxo anions such as: ADP and ATP





### Polyoxo anions and extended covalent structures





# $2 PO_4^{3-} + 2 H_3^{0+} \longrightarrow P_2^{0}O_7^{4-} + 3 H_2^{0}O_7^{0-}$





### Allotropes of phosphorus





# White, red and black phosphorus



White phosphorus

Terrible burns; used in weapons In despicable wars.







**BP** (Black phosphorus)



Lewis approach to acid/base interactions



Boron trifluoride-ammonia adduct





Gilbert Newton Lewis 1875 – 1946



# Lewis Concept

Lewis, 1930s:

## Base is a donor of an electron pair.

# Acid is an acceptor of an electron pair.

For a species to function as a Lewis acid, it needs to have an accessible empty orbital.

For a species to function as a Lewis base it needs to have an accessible electron pair.

Examples of Lewis acids: **BF**<sub>3</sub>, **AICI**<sub>3</sub>, **SbF**<sub>5</sub>, **Na+**, **H+**, **S**<sup>6+</sup>, etc.

Examples of Lewis bases: **F**<sup>-</sup>, **H**<sub>2</sub>**O**, **Me**<sub>3</sub>**N**, **C**<sub>2</sub>**H**<sub>4</sub>, **Xe**, etc.

# Lewis Continued

A more general view also classifies compounds that can generate a species with an empty orbital as Lewis acids. Then we can include  $B_2H_6$ ,  $AI_2CI_6$ , HCI etc.

Since H<sup>+</sup> and any cation from a solvent autodissociation is a Lewis acid, and anything that can add H<sup>+</sup> or a solventderived cation is a Lewis base, the Lewis acid concept effectively includes the ones discussed previously.

# Lewis Continued

Acid-base reactions under the Lewis model are the reactions of forming adducts between Lewis acids and bases.

 $BF_{3} + Me_{3}N \rightarrow F_{3}B-NMe_{3}$   $HF + F^{-} \rightarrow FHF^{-}$   $SiF_{4} + 2F^{-} \rightarrow SiF_{6}^{2-}$   $CO_{2} + OH^{-} \rightarrow HCO_{3}^{-}$  $TiCl_{4} + 2Et_{2}O \rightarrow TiCl_{4}(OEt_{2})_{2}$ 

In fact, any chemical compound can be mentally disassembled into Lewis acids and bases:

S<sup>6+</sup> + 6F<sup>-</sup> → SF<sub>6</sub> C<sup>4+</sup> + 3H<sup>-</sup> + NH<sub>2</sub><sup>-</sup> → CH<sub>3</sub><sup>+</sup> + NH<sub>2</sub><sup>-</sup>

# Lewis Acids & Bases

Other good examples involve metal ions.



# Lewis Acids & Bases

The combination of metal ions (Lewis acids) with Lewis bases such as H<sub>2</sub>O and NH<sub>3</sub> -----> COMPLEX IONS

All metal ions form complex ions with water —and are of the type  $[M(H_2O)_x]^{n+}$  where x = 4 and 6.





# Lewis Acids & Bases

Add  $NH_3$  to light blue  $[Cu(H_2O)_4]^{2+}$  -----> light blue  $Cu(OH)_2$  and then deep blue  $[Cu(NH_3)_4]^{2+}$ 





# Hard-Soft Acid Base "Theory"

The classification of the stabilities metal ions and ligands is derived using Hard and soft Lewis acid-base theory (HSAB).

The terms hard and soft refer to a hard shell of tightly held electrons and a soft shell of polarisable electrons, respectively.

The theory is both empirical (i.e. based on experimental observation) and theoretical Rule:

HARD likes HARD, and SOFT likes SOFT

- hard-hard are known as ion-pairs
- K increases with cation charge
- K increases with decreasing radius
- soft-soft is covalent: K trends irregular
- Rule:

hard-hard is WEAKER than soft-soft

Rule:

HARD acid – SOFT base is NEGLIGIBLE

# HSAB Classification of Acids and Bases

0	r	d	
a	L	u	

ACIDS H<sup>+</sup>, Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>+</sup>, Ag<sup>+</sup>, Au<sup>+</sup>, Tl<sup>+</sup>, Rb<sup>+</sup>, Cs<sup>+</sup>, Be<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Hg<sup>+</sup>, Pd<sup>2+</sup>, Cd<sup>2+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Ba<sup>2+</sup>, SO<sub>2</sub>, BBr<sub>3</sub>. Cr3+, SO3, BF3. BASES F, OH, H,O, NH, CO32, NO3, O2, CI, C6H5N, SCN R3P, C6H6, R2S SO42-, PO43-, CIO4-.

### Borderline

## Soft

Pt<sup>2+</sup>, Hg<sup>2+</sup>, BH<sub>3</sub>.

NO<sub>2</sub><sup>-</sup>, SO<sub>3</sub><sup>2-</sup>, N<sub>3</sub><sup>-</sup> H<sup>-</sup>, R<sup>-</sup>, CN<sup>-</sup>, CO, I<sup>-</sup>,

Classification of Bases			
Hard	Soft		
H <sub>2</sub> O, OH <sup>-</sup> , F <sup>-</sup>	R <sub>2</sub> S, RSH, RS <sup>-</sup>		
CH <sub>3</sub> CO <sub>2</sub> <sup>-</sup> , PO <sub>4</sub> <sup>3-</sup> , SO <sub>4</sub> <sup>2-</sup>	I <sup>-</sup> , SCN <sup>-</sup> , S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>		
Cl <sup>-</sup> , CO <sub>3</sub> <sup>2-</sup> , ClO <sub>4</sub> <sup>-</sup> , NO <sub>3</sub> <sup>-</sup>	$R_3P$ , $R_3As$ , $(RO)_3P$		
ROH, $RO^-$ , $R_2O$	CN <sup>-</sup> , RNC, CO		
NH <sub>3</sub> , RNH <sub>2</sub> , N <sub>2</sub> H <sub>4</sub>	$C_2H_4, C_6H_6$		
	H−, <b>R</b> −		
Borde	erline		
C <sub>6</sub> H <sub>5</sub> NH <sub>2</sub> , C <sub>5</sub> H <sub>5</sub> N, N <sub>3</sub> <sup>-</sup>	, Br <sup>-</sup> , NO <sub>2</sub> <sup>-</sup> , SO <sub>3</sub> <sup>2-</sup> , N <sub>2</sub>		

#### Classification of Lewis Acids

Class (a)/Hard	Class (b)/Soft
H <sup>+</sup> , Li <sup>+</sup> , Na <sup>+</sup> , K <sup>+</sup>	Cu <sup>+</sup> , Ag <sup>+</sup> , Au <sup>+</sup> , Tl <sup>+</sup> , Hg <sup>+</sup> , Cs <sup>+</sup>
Be <sup>2+</sup> , Mg <sup>2+</sup> , Ca <sup>2+</sup> , Sr <sup>2+</sup> , Sn <sup>2+</sup>	Pd <sup>2+</sup> , Cd <sup>2+</sup> , Pt <sup>2+</sup> , Hg <sup>2+</sup>
Al <sup>3+</sup> , Se <sup>3+</sup> , Ga <sup>3+</sup> , In <sup>3+</sup> , La <sup>3+</sup>	CH <sub>3</sub> Hg <sup>+</sup>
Cr <sup>3+</sup> , Co <sup>3+</sup> , Fe <sup>3+</sup> , As <sup>3+</sup> , Ir <sup>3+</sup>	Tl <sup>3+</sup> , Tl(CH <sub>3</sub> ) <sub>3</sub> , RH <sub>3</sub>
Si <sup>4+</sup> , Ti <sup>4+</sup> , Zr <sup>4+</sup> , Th <sup>4+</sup> , Pu <sup>4+</sup> , VO <sup>2+</sup>	RS <sup>+</sup> , RSe <sup>+</sup> , RTe <sup>+</sup>
UO <sub>2</sub> <sup>2+</sup> , (CH <sub>3</sub> ) <sub>2</sub> Sn <sup>2+</sup>	I <sup>+</sup> , Br <sup>+</sup> , HO <sup>+</sup> , RO <sup>+</sup>
BeMe <sub>2</sub> , BF <sub>3</sub> , BCl <sub>3</sub> , B(OR) <sub>3</sub>	I <sub>2</sub> , Br <sub>2</sub> , INC, etc.
Al(CH <sub>3</sub> ) <sub>3</sub> , Ga(CH <sub>3</sub> ) <sub>3</sub> , In(CH <sub>3</sub> ) <sub>3</sub>	Trinitrobenzene, etc.
RPO <sub>2</sub> <sup>+</sup> , ROPO <sub>2</sub> <sup>+</sup>	Chloranil, quinones, etc.
RSO <sub>2</sub> <sup>+</sup> , ROSO <sub>2</sub> <sup>+</sup> , SO <sub>3</sub>	Tetracyanoethylene, etc.
$I^{7+}, I^{5+}, Cl^{7+}$	O, Cl, Br, I, R <sub>3</sub> C
$R_3C^+$ , $RCO^+$ , $CO_2$ , $NC^+$	M <sup>0</sup> (metal atoms) Bulk metals

HX (hydrogen-bonding molelcules) Borderline Fe<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup> B(CH<sub>3</sub>)<sub>3</sub>, SO<sub>2</sub>, NO<sup>+</sup>

# Pearson's HSAB Classification of Heavy Metal Lewis Acids HARD: Cr<sup>3+</sup> Co<sup>3+</sup> Fe<sup>3+</sup> Ti<sup>4+</sup> Ce<sup>3+</sup> Sn<sup>4+</sup>

 ${\bf Borderline: Fe^{2+} \ Co^{2+} \ Ni^{2+} \ Cu^{2+} \ Zn^{2+} \ Pb^{2+} \ Sn^{2+} \$ 

SOFT: Cu<sup>+</sup> Ag<sup>+</sup> Au<sup>+</sup> Tl<sup>+</sup> Hg<sup>+</sup> Pd<sup>2+</sup> Cd<sup>2+</sup> Pt<sup>2+</sup> Hg<sup>2+</sup> Tl<sup>3+</sup> M<sup>0</sup> (metal atoms) and bulk metals

#### HSAB is particularly useful in Coordination Chemistry of Transition Metals

Metal ions (Lewis acids) can be divided into two categorie (hard and soft) according to type of ligand (Lewis base) to prefer i.e. that form the most stable complex with

Pearson's HSAB Classification of Heavy Metal Lewis Acids

HARD: Cr<sup>3+</sup> Co<sup>3+</sup> Fe<sup>3+</sup> Ti<sup>4+</sup> Ce<sup>3+</sup> Sn<sup>4+</sup>

Borderline: Fe<sup>2+</sup> Co<sup>2+</sup> Ni<sup>2+</sup> Cu<sup>2+</sup> Zn<sup>2+</sup> Pb<sup>2+</sup> Sn<sup>2+</sup>

- Hard Lewis acids have either a noble gas configuration or high charge, and therefore strongly-held electrons, and prefer hard Lewis bases
- Soft Lewis acids have a large number of d electrons and low charge, and therefore more polarisable electrons, and prefer soft Lewis bases.