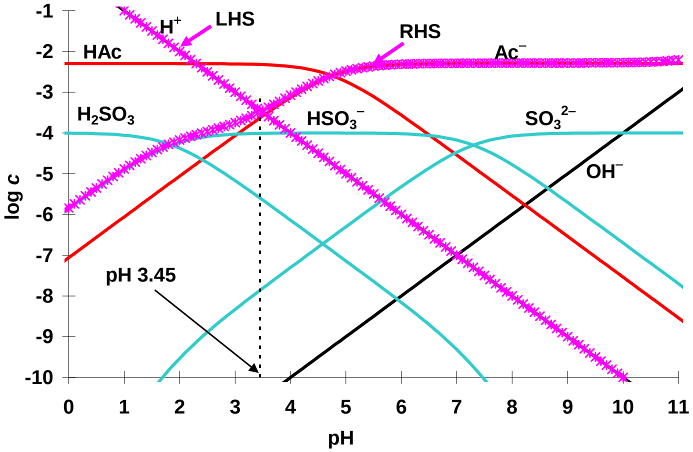
Graphical Solution of Acid/Base Problems



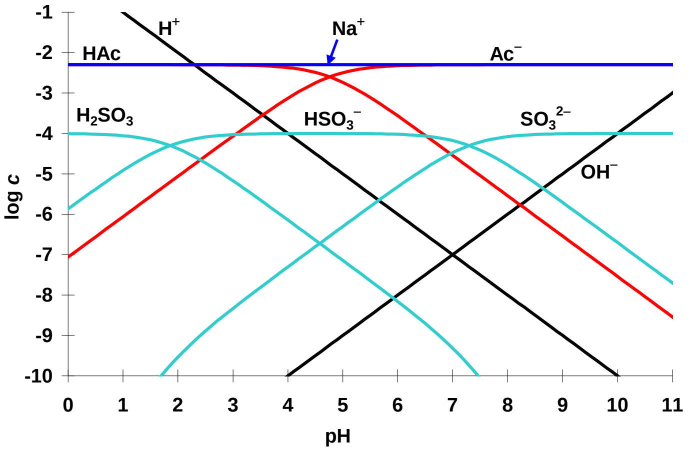
Graphical Solution of Acid/Base Problems

Example: Speciation of $10^{-4.0}$ *M* H_2SO_3 + $10^{-2.3}$ *M* NaAc

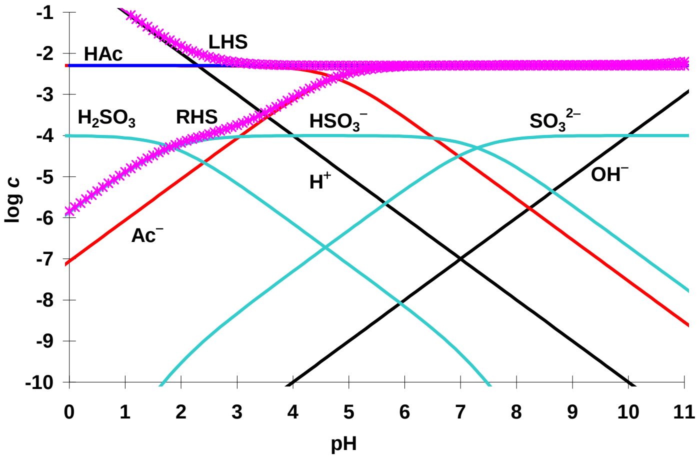
- Species: H^+, OH^-, H_2SO_3, HSO_3^-, SO_3^{2-}, HAc, Ac^-, Na^+
- Equilibrium constants
  - (*a*) $K_w = 10^{-14.0}$
  - (*b*) $K_{a1,S} = 10^{-1.86}$, $K_{a2,S} = 10^{-7.30}$, $K_{a,Ac} = 10^{-4.76}$
  - (*c*) N/A
  - (*d*) None
- Mass balances: $TOTSO_3=10^{-4.0}$, $TOTNa=TOTAc=10^{-2.3}$
- Charge balance:

$$[Na^+] + [H^+] = [OH^-] + [HSO_3^-] + 2[SO_3^{2-}] + [Ac^-]$$

Graphical Solution of Acid/Base Problems



Graphical Solution of Acid/Base Problems



Graphical Solution of Acid/Base Problems

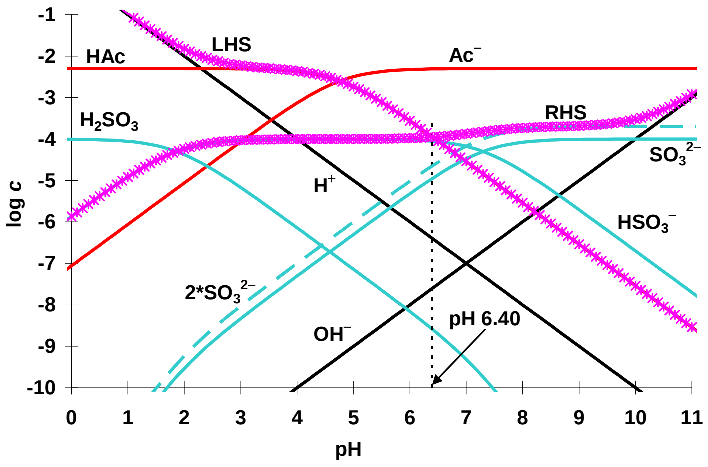
Modify CB to eliminate the ‘big number’ on each side of the equation, by subtracting a value equal to that ‘big number’.

$$[Na^+] + [H^+] = [OH^-] + [HSO_3^-] + 2[SO_3^{2-}] + [Ac^-]$$

$$-\left([Na^+] = [HAc] + [Ac^-]\right)$$

$$[HAc] + [H^+] = [OH^-] + [HSO_3^-] + 2[SO_3^{2-}]$$

Graphical Solution of Acid/Base Problems



Summary: Graphical Solution of Acid/Base Problems

Graphical analysis is a relatively fast, convenient way to estimate the speciation of acid/base systems. It is most useful when:

- The *TOTc* values are known, but the pH is not
- We wish to consider the speciation in several different systems, all with similar *TOTc* values
- The species in the CB are all non-dominant species

Making Graphical Solution of Acid/Base Problems More Efficient

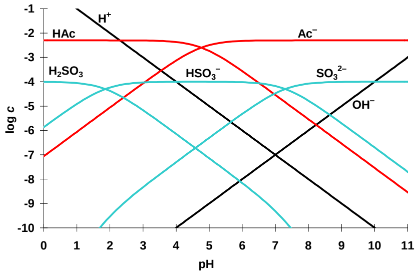
How can we write a modified CB containing only non-dominant species directly? Two steps:

1. **Identify anticipated dominant species.**
2. **Determine how to write modified CB that doesn’t contain those species (even if they have charge).**

Predicting Dominant Species

- As the pH drops from pK_a+1 to pK_a–1, almost all of each $H_nA/H_{n-1}A$ conjugate pair changes from deprotonated to protonated, thereby consuming *TOTA* 'available H^+'
- Stronger bases become protonated at higher pH than weaker bases

All available, exchangeable H^+ ions are used to protonate available bases, from strongest (highest pK_a) to weakest. This process continues until no available, exchangeable H^+ remains.



Example: Speciation of $10^{-4.0}$ *M* H_2SO_3 + $10^{-2.3}$ *M* NaAc

Input in terms of bases and exchangeable H^+:

$10^{-4.0}$ SO_3^{2-} (pK_{a2}=7.2, pK_{a1}=2.08) ***plus***

$10^{-2.3}$ (i.e., 5x10^{-3}) Ac^- (pK_{a1}=4.76) ***plus***

2*10^{-4} exchangeable H^+

Imagined protonation sequence:

- $10^{-4.0}$ H^+ to convert all SO_3^{2-} to HSO_3^-; 10^{-4} H^+ remains
- $10^{-4.0}$ H^+ to convert 2% of Ac^- to HAc
- No exchangeable H^+ remains

Conclusion: HSO_3^- and Ac^- likely to be dominant

$10^{-4.0}$ *M* H_2SO_3 + $10^{-2.3}$ *M* NaAc

Imagined protonation sequence:

pK_a	Conversion	Available H^+	Main Ac Species	Main SO_3 Species
--	*Initial Condition*	2.0x10^{-4}	Ac^-	SO_3^{2-}
7.30	$SO_3^{2-} \rightarrow HSO_3^-$	1.0x10^{-4}	Ac^-	HSO_3^-
4.76	$Ac^- \rightarrow HAc$	0.0	Ac^-	HSO_3^-
1.86	$HSO_3^- \rightarrow H_2SO_3$			

Example: 4x10^{-4} Na_2CO_3 + 10^{-4} $NaHCO_3$ + 10^{-3} NaH_2PO_4 + 3*10^{-3} HCl

Input in terms of bases and exchangeable H^+:

5x10^{-4} CO_3^{2-} (pK_{a2}=10.33, pK_{a1}=6.35) ***plus***

10^{-3} PO_4^{3-} (pK_{a3}=12.35, pK_{a2}=7.20, pK_{a1}=2.16) ***plus***

5.1*10^{-3} exchangeable H^+

$4\text{x}10^{-4}\ Na_2CO_3 + 10^{-4}\ NaHCO_3 + 10^{-3}\ NaH_2PO_4 + 3{*}10^{-3}\ HCl$

Imagined protonation sequence:

pK_a	Conversion	Available H^+	Main CO_3 Species	Main PO_4 Species
--	*Initial Condition*	$5.1\text{x}10^{-3}$	CO_3^{2-}	PO_4^{3-}
12.35	$PO_4^{3-} \to HPO_4^{2-}$	$4.1\text{x}10^{-3}$	CO_3^{2-}	HPO_4^{2-}
10.33	$CO_3^{2-} \to HCO_3^-$	$3.6\text{x}10^{-3}$	HCO_3^-	HPO_4^{2-}
7.20	$HPO_4^{2-} \to H_2PO_4^-$	$2.6\text{x}10^{-3}$	HCO_3^-	$H_2PO_4^-$
6.35	$HCO_3^- \to H_2CO_3$	$2.1\text{x}10^{-3}$	H_2CO_3	$H_2PO_4^-$
2.16	$H_2PO_4^- \to H_3PO_4$	$1.1\text{x}10^{-3}$	H_2CO_3	H_3PO_4

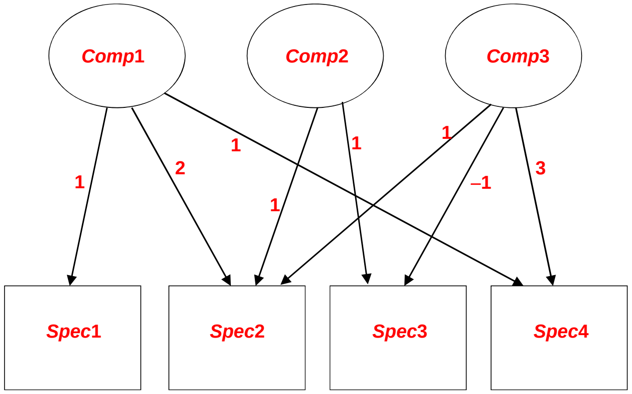
Making Graphical Solution of Acid/Base Problems More Efficient

How can we write a modified CB containing only non-dominant species directly? Two steps:

1. **Identify anticipated dominant species.**
2. **Determine how to write modified CB that doesn't contain those species (even if they have charge).**

   Approach: Write a modified mass balance on H^+ – the '*TOT*H equation'

Components, Species, and the System Tableau



__*Comp*1 + __*Comp*2 + __*Comp*3 + … → $\underline{1}$ *Spec*1

***Example*: $3\text{x}10^{-4}\ H_3PO_4$**

Reaction Written Conventionally		Reaction Forming *Species* from *Components* (H_2O, H^+, PO_4^{3-})	
$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-$	K_{a1}	$\underline{3}\ H^+ + \underline{1}\ PO_4^{3-} \leftrightarrow \underline{1}\ H_3PO_4$	$(K_{a1}K_{a2}K_{a3})^{-1}$
$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-}$	K_{a2}	$\underline{2}\ H^+ + \underline{1}\ PO_4^{3-} \leftrightarrow \underline{1}\ H_2PO_4^-$	$(K_{a2}K_{a3})^{-1}$
$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}$	K_{a3}	$\underline{1}\ H^+ + \underline{1}\ PO_4^{3-} \leftrightarrow \underline{1}\ HPO_4^{2-}$	$(K_{a3})^{-1}$
$PO_4^{3-} \leftrightarrow PO_4^{3-}$	$K=1$	$\underline{1}\ PO_4^{3-} \leftrightarrow \underline{1}\ PO_4^{3-}$	$K=1$
$H^+ \leftrightarrow H^+$	$K=1$	$\underline{1}\ H^+ \leftrightarrow \underline{1}\ H^+$	$K=1$
$H_2O \leftrightarrow H^+ + OH^-$	K_w	$\underline{1}\ H_2O - \underline{1}\ H^+ \leftrightarrow \underline{1}\ OH^-$	K_w
$H_2O \leftrightarrow H_2O$	$K=1$	$\underline{1}\ H_2O \leftrightarrow \underline{1}\ H_2O$	$K=1$

$\log(H_3PO_4) = \log(H_2O)^0 + \log(H^+)^3 + \log(PO_4^{3-})^1 + \log(K_{a1}K_{a2}K_{a3})^{-1}$

$\log(H_2PO_4^-) = \log(H_2O)^0 + \log(H^+)^2 + \log(PO_4^{3-})^1 + \log(K_{a2}K_{a3})^{-1}$

$\log(HPO_4^{2-}) = \log(H_2O)^0 + \log(H^+)^1 + \log(PO_4^{3-})^1 + \log(K_{a3})^{-1}$

$\log(PO_4^{3-}) = \log(H_2O)^0 + \log(H^+)^0 + \log(PO_4^{3-})^1 + \log(1)$

$\log(H^+) = \log(H_2O)^0 + \log(H^+)^1 + \log(PO_4^{3-})^0 + \log(1)$

$\log(OH^-) = \log(H_2O)^1 + \log(H^+)^{-1} + \log(K_w)$

$\log(H_2O) = \log(H_2O)^1 + \log(H^+)^0 + \log(1)$

$\log(H_3PO_4) = \log(H_2O)^0 + \log(H^+)^3 + \log(PO_4^{3-})^1 + \log(K_{a1}K_{a2}K_{a3})^{-1}$

$\log(H_2PO_4^-) = \log(H_2O)^0 + \log(H^+)^2 + \log(PO_4^{3-})^1 + \log(K_{a2}K_{a3})^{-1}$

$\log(HPO_4^{2-}) = \log(H_2O)^0 + \log(H^+)^1 + \log(PO_4^{3-})^1 + \log(K_{a3})^{-1}$

$\log(PO_4^{3-}) = \log(H_2O)^0 + \log(H^+)^0 + \log(PO_4^{3-})^1 + \log(1)$

$\log(H^+) = \log(H_2O)^0 + \log(H^+)^1 + \log(PO_4^{3-})^0 + \log(1)$

$\log(OH^-) = \log(H_2O)^1 + \log(H^+)^{-1} + \log(PO_4^{3-})^0 + \log(K_w)$

$\log(H_2O) = \log(H_2O)^1 + \log(H^+)^0 + \log(PO_4^{3-})^0 + \log(1)$

$\log(H_3PO_4) = 0\log(H_2O) + 3\log(H^+) + 1\log(PO_4^{3-})^1 + \log(K_{a1}K_{a2}K_{a3})^{-1}$

$\log(H_2PO_4^-) = 0\log(H_2O) + 2\log(H^+) + 1\log(PO_4^{3-}) + \log(K_{a2}K_{a3})^{-1}$

$\log(HPO_4^{2-}) = 0\log(H_2O) + 1\log(H^+) + 1\log(PO_4^{3-}) + \log(K_{a3})^{-1}$

$\log(PO_4^{3-}) = 0\log(H_2O) + 0\log(H^+) + 1\log(PO_4^{3-})^1 + \log(1)$

$\log(H^+) = 0\log(H_2O) + 1\log(H^+) + 0\log(PO_4^{3-}) + \log(1)$

$\log(OH^-) = 1\log(H_2O) - 1\log(H^+) + 0\log(PO_4^{3-}) + \log(K_w)$

$\log(H_2O) = 1\log(H_2O) + 0\log(H^+) + 0\log(PO_4^{3-}) + \log(1)$

***Example*: 3x10^{-4} H_3PO_4**

	H_2O	H^+	PO_4^{3-}	log K
H_3PO_4	0	3	1	$\log(K_{a1}K_{a2}K_{a3})^{-1}$
$H_2PO_4^-$	0	2	1	$\log(K_{a2}K_{a3})^{-1}$
HPO_4^{2-}	0	1	1	$\log(K_{a3})^{-1}$
PO_4^{3-}	0	0	1	log (1) = 0
H^+	0	1	0	log (1) = 0
OH^-	1	–1	0	$\log K_w$
H_2O	1	0	0	log (1) = 0

This table contains all the information in the equilibrium constant relationships. Next, add information in the mass balances.

Equilibrium Species Tableau

Example: 3x10^{-4} H_3PO_4

	H_2O	H^+	PO_4^{3-}	log K	Conc'n
H_3PO_4	0	3	1	21.71	$[H_3PO_4]_{eq}$
$H_2PO_4^-$	0	2	1	19.55	$[H_2PO_4^-]_{eq}$
HPO_4^{2-}	0	1	1	12.35	$[HPO_4^{2-}]_{eq}$
PO_4^{3-}	0	0	1	0	$[PO_4^{3-}]_{eq}$
H^+	0	1	0	0	$[H^+]_{eq}$
OH^-	1	–1	0	–14.0	$[OH^-]_{eq}$
H_2O	1	0	0	0	$[H_2O]_{eq}$
	$TOTH_2O_{eq}$	$TOTH_{eq}$	$TOTPO_{4,eq}$		

$$TOT\mathbf{H_2O}_{eq} = [H_2O]_{eq} + [OH^-]_{eq}$$

$$TOT\mathbf{H}_{eq} = 3[H_3PO_4]_{eq} + 2[H_2PO_4^-]_{eq} + [HPO_4^{2-}]_{eq} + [H^+]_{eq} - [OH^-]_{eq}$$

$$TOT\mathbf{PO_4}_{,eq} = [H_3PO_4]_{eq} + [H_2PO_4^-]_{eq} + [HPO_4^{2-}]_{eq} + [PO_4^{3-}]_{eq}$$