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	$[H_2O]_{eq}$
	$TOTH_2O_{eq}$	$TOTH_{eq}$	$TOTPO_{4,eq}$		

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

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

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

Input Species Tableau

- The ***components*** in the equilibrium ***species*** must have been available in the ***inputs*** to the system, so it must be possible to express the ***inputs*** in terms of ***components***.

Example: 3x10^{-4} H_3PO_4

	H_2O	H^+	PO_4^{3-}	Conc'n
H_3PO_4	0	3	1	3x10^{-4}
H_2O	1	0	0	55.56
	$TOTH_2O_{in}$	$TOTH_{in}$	$TOTPO_{4,in}$	

$$TOT\mathbf{H_2O}_{in} = [\mathrm{H_2O}]_{in} + [\mathrm{OH^-}]_{in} = 55.56$$

$$TOT\mathbf{H}_{eq} = 3[\mathrm{H_3PO_4}]_{eq} = 9\mathrm{x}10^{-4}$$

$$TOT\mathbf{PO_4}_{,eq} = [\mathrm{H_3PO_4}]_{in} = 3\mathrm{x}10^{-4}$$

Mass Balances Based on Tableaus

- ***Components*** are conserved. The total concentration of each component must be the same in the ***inputs*** and equilibrium ***species***.

$$TOT\mathbf{H_2O}_{eq} = TOT\mathbf{H_2O}_{in}$$

$$[\mathrm{H_2O}]_{eq} + [\mathrm{OH^-}]_{eq} = 55.56$$

$$TOT\mathbf{H}_{eq} = TOT\mathbf{H}_{in}$$

$$3[\mathrm{H_3PO_4}]_{eq} + 2[\mathrm{H_2PO_4^-}]_{eq} + [\mathrm{HPO_4^{2-}}]_{eq} + [\mathrm{H^+}]_{eq} - [\mathrm{OH^-}]_{eq} = 9\mathrm{x}10^{-4}$$

$$TOT\mathbf{PO_4}_{,eq} = TOT\mathbf{PO_4}_{,eq}$$

$$3\mathrm{x}10^{-4} = [\mathrm{H_3PO_4}]_{eq} + [\mathrm{H_2PO_4^-}]_{eq} + [\mathrm{HPO_4^{2-}}]_{eq} + [\mathrm{PO_4^{3-}}]_{eq}$$

- Every ***species*** expected to be present in the equilibrium solution is included in the list, expressed in terms of the ***components*** that it comprises
- The table implicitly includes an equation for the total concentration of each ***component*** in the equilibrium solution (***$TOTi_{eq}$***)
- The ***components*** in the equilibrium ***species*** must have been available in the ***inputs*** to the system, so it must be possible to express the ***inputs*** in terms of ***components***.
- ***Components*** are conserved. The total concentration of each component must be the same in the ***inputs*** and equilibrium ***species***
- '***Inputs'*** can be interpreted literally or as a combination of the composition at some prior time plus all chemicals that entered subsequently

Key Results

- Each ***component*** appears in the mass balance on itself (***$TOTi_{in}$ = $TOTi_{eq}$***), but not in any other mass balance. Therefore, the *TOT*H equation has terms for $[H^+]$ and concentrations of various other ***species***, but not for other ***components***.
- The *TOT*H equation is a (modified) mass balance, so it must be satisfied at equilibrium.
- If we choose dominant species as ***components***, the *TOT*H equation (***$TOTH_{in}$ = $TOTH_{eq}$***) will include only terms for non-dominant ***species***. It therefore meets our objectives for direct use with a log *c* – pH diagram to solve for equilibrium speciation.

Graphical/TOT*H* Solution of Acid/Base Problems

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^+

$10^{-4.0}$ *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	$HSO_3^- \rightarrow H_2SO_3$			

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

	H_2O	H^+	Ac^-	HSO_3^-	Na^+	log *K*
HSO_3^-	0	0	0	1	0	0
H_2SO_3	0	1	0	1	0	1.86
SO_3^{2-}	0	–1	0	1	0	–7.30
Ac^-	0	0	1	0	0	0
HAc	0	1	1	0	0	4.76
H^+	0	1	0	0	0	0
OH^-	1	–1	0	0	0	–14.0
H_2O	1	0	0	0	0	0
Na^+	0	0	0	0	1	0
	$TOTH_2O_{eq}$	$TOTH_{eq}$	$TOTAc_{,eq}$	$TOTSO_3$	*TOT*Na	

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

$$TOT\mathbf{Na}_{eq} = [Na^+]_{eq} \qquad TOT\mathbf{SO}_{3,eq} = [H_2SO_3]_{eq} + [HSO_3^-]_{eq} + [SO_3^{2-}]_{eq}$$

$$TOT\mathbf{H}_{eq} = [H^+]_{eq} - [OH^-]_{eq} + [H_2SO_3]_{eq} - [SO_3^{2-}]_{eq} + [HAc]$$

Input Species Tableau

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

	H_2O	H^+	Ac^-	HSO_3^-	Na^+	Conc'n
H_2O	1	0	0	0	0	55.56
H_2SO_3	0	1	0	1	0	10^{-4}
NaAc	0	0	1	0	1	$10^{-2.3}$
	$TOTH_2O_{in}$	$TOTH_{in}$	$TOTAc_{in}$	$TOTSO_{3,in}$	$TOTNa_{in}$	

$$TOT\mathbf{H_2O}_{in} = [\mathrm{H_2O}]_{in} = 55.56$$

$$TOT\mathbf{H}_{in} = [\mathrm{H_2SO_3}]_{in} = 10^{-4.0}$$

$$TOT\mathbf{Ac}_{in} = [\mathrm{NaAc}]_{in} = 10^{-2.3}$$

$$TOT\mathbf{SO}_{3,in} = [\mathrm{H_2SO_3}]_{in} = 10^{-4.0}$$

$$TOT\mathbf{Na}_{in} = [\mathrm{NaAc}]_{in} = 10^{-2.3}$$

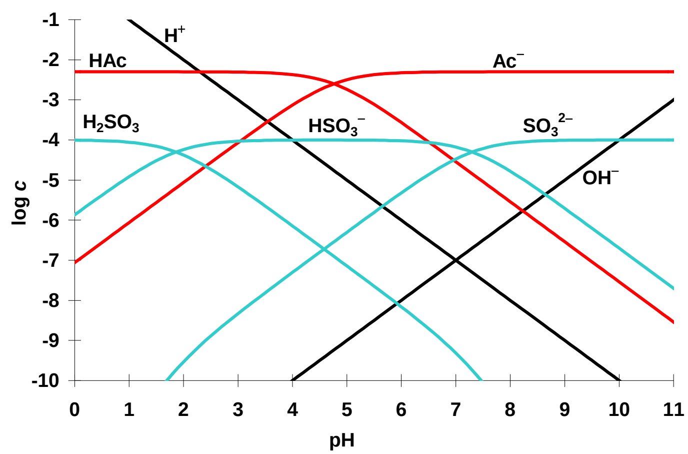
Graphical/TOT*H* Solution of Acid/Base Problems

$$TOT\mathbf{H}_{eq} = TOT\mathbf{H}_{in}$$

$$[\mathrm{H^+}]_{eq} - [\mathrm{OH^-}]_{eq} + [\mathrm{H_2SO_3}]_{eq} - [\mathrm{SO_3^{2-}}]_{eq} + [\mathrm{HAc}] = 10^{-4.0}$$

$$[\mathrm{H^+}] + [\mathrm{HAc}] + [\mathrm{H_2SO_3}] = [\mathrm{OH^-}] + [\mathrm{SO_3{}^{2-}}] + 10^{-4.0}$$

Graphical Solution of Acid/Base Problems



Graphical Solution of Acid/Base Problems