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

Example: 4×10^{-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^+:

5×10^{-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^+

4×10^{-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*	5.1×10^{-3}	CO_3^{2-}	PO_4^{3-}
12.35	$PO_4^{3-}\rightarrow HPO_4^{2-}$	4.1×10^{-3}	CO_3^{2-}	HPO_4^{2-}
10.33	$CO_3^{2-}\rightarrow HCO_3^-$	3.6×10^{-3}	HCO_3^-	HPO_4^{2-}
7.20	$HPO_4^{2-}\rightarrow H_2PO_4^-$	2.6×10^{-3}	HCO_3^-	$H_2PO_4^-$
6.35	$HCO_3^-\rightarrow H_2CO_3$	2.1×10^{-3}	H_2CO_3	$H_2PO_4^-$
2.16	$H_2PO_4^-\rightarrow H_3PO_4$	1.1×10^{-3}	H_2CO_3	H_3PO_4

Equilibrium Species Tableau

4×10^{-4} Na_2CO_3 +10^{-4} $NaHCO_3$ +10^{-3} NaH_2PO_4 + 3*10^{-3} HCl

	H_2O	H^+	H_3PO_4	H_2CO_3	Na^+	Cl^-	log *K*
H_3PO_4	0	0	1	0	0	0	0
$H_2PO_4^-$	0	–1	1	0	0	0	–2.16
HPO_4^{2-}	0	–2	1	0	0	0	–7.20
PO_4^{3-}	0	–3	1	0	0	0	–21.71
H_2CO_3	0	0	0	1	0	0	0
HCO_3^-	0	–1	0	1	0	0	–6.35
CO_3^{2-}	0	–2	0	1	0	0	–16.68
Na^+	0	0	0	0	1	0	0
Cl^-	0	0	0	0	0	1	0
H^+	0	1	0	0	0	0	0
OH^-	1	–1	0	0	0	0	–14.00
H_2O	1	0	0	0	0	0	0

Input Species Tableau

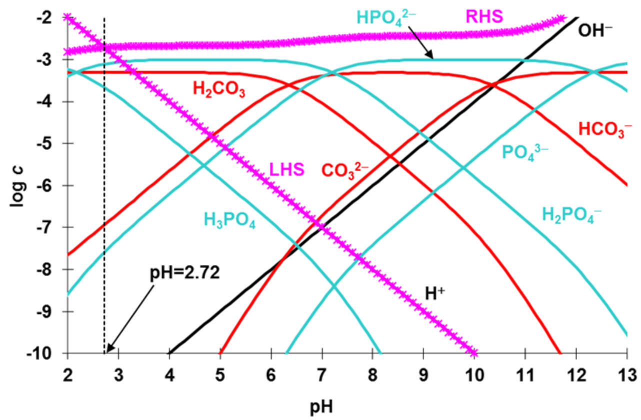
4×10^{-4} Na_2CO_3 +10^{-4} $NaHCO_3$ +10^{-3} NaH_2PO_4 + 3×10^{-3} HCl

	H_2O	H^+	H_3PO_4	H_2CO_3	Na^+	Cl^-	Conc'n
NaH_2PO_4	0	–1	1	0	1	0	10^{-3}
Na_2CO_3	0	–2	0	1	2	0	4×10^{-4}
$NaHCO_3$	0	–1	0	1	1	0	10^{-4}
HCl	0	1	0	0	0	1	3×10^{-3}
H_2O	1	0	0	0	0	0	55.56
TOTi	55.56	1.1×10^{-3}	10^{-3}	5.0×10^{-4}	1.9×10^{-3}	3.0×10^{-3}	

$$1.1\times10^{-3} = \left[H^+\right]-\left[OH^-\right]-3\left[PO_4^{3-}\right]-2\left[HPO_4^{2-}\right]-\left[H_2PO_4^-\right]-2\left[CO_3^{2-}\right]-\left[HCO_3^-\right]$$

$$\left[H^+\right] = 1.1\times10^{-3}+\left[OH^-\right]+3\left[PO_4^{3-}\right]+2\left[HPO_4^{2-}\right]+\left[H_2PO_4^-\right]+2\left[CO_3^{2-}\right]+\left[HCO_3^-\right]$$

$4x10^{-4}\ Na_2CO_3 + 10^{-4}\ NaHCO_3 + 10^{-3}\ NaH_2PO_4 + 3x10^{-3}\ HCl$



Summary: The *TOT*H Equation

- The *TOT*H equation is a mole balance on H^+, stating that the concentration of **H^+** 'component units' in the input must equal that in the species present at equilibrium.
- The number of **H^+** units in an input or equilibrium species depends on the choice for the component set. Many choices for this set are acceptable, as long as they meet certain criteria.
- All species in the initial system and all subsequent inputs must be considered to determine $TOTH_{in}$; all species in the equilibrium solution must be considered to determine $TOTH_{eq}$.
- The likely dominant equilibrium species can be determined based on the idea that solutions have no memory. Choosing these species as the components eliminates them from the *TOT*H equation.

Chemical Equilibrium Modeling

Generic Approach for Solving Acid/Base Problems

- *Input information needed to prepare tableau*
- *Guess the activities of the* ***components***
- *Use equilibrium expressions, as embedded in the tableau, to compute the activity of each* ***species***
- *Estimate ionic strength and activity coefficients, and use these to compute concentrations of the* ***components***
- *Use mass balance expressions, as embedded in the tableau, to test whether the guesses of* ***component*** *activities are correct*
- *Based on the magnitude of the errors in the MBs, make better guesses for the* ***component*** *activities; continue until errors in MBs are satisfactorily small*

Chemical Equilibrium Modeling

Example: $3x10^{-4}\ H_3PO_4$; assume ideal solution

Choices for components: **H_2O, H^+, PO_4^{3-}**

	H_2O	H^+	PO_4^{3-}	log *K*
H_3PO_4	0	3	1	21.71
$H_2PO_4^-$	0	2	1	19.55
HPO_4^{2-}	0	1	1	12.35
PO_4^{3-}	0	0	1	0
H^+	0	1	0	0
OH^-	1	–1	0	–14.0
H_2O	1	0	0	0
	55.56	$9x10^{-4}$	$3x10^{-4}$	

Guesses for first iteration: **$(H_2O)=1.0$, $(H^+)=10^{-7.0}$, $(PO_4^{3-})=10^{-10.0}$**

Guesses for first iteration: **(H_2O)=1.0, (H^+)=$10^{-7.0}$, (PO_4^{3-})=$10^{-10.0}$**

log (H_3PO_4)	=	3(–7.0) + 1(–10.0) + 21.71 = –9.29
log ($H_2PO_4^-$)	=	2(–7.0) + 1(–10.0) + 19.55 = –4.45
log (HPO_4^{2-})	=	1(–7.0) + 1(–10.0) + 12.35 = –4.65
log (PO_4^{3-})	=	1(–10.0) = –10.0
log (H^+)	=	1(–7.0) = –7.0
log (OH^-)	=	1(0) – 1(–7.0) + (–14.0) = –7.0
log (H_2O)	=	1(0) = 0

TOT*PO$_4$ *equation:

$$\left[\mathrm{H_3PO_4}\right]_{eq} + \left[\mathrm{H_2PO_4^-}\right]_{eq} + \left[\mathrm{HPO_4^{2-}}\right]_{eq} + \left[\mathrm{PO_4^{3-}}\right]_{eq} = 5.79\text{x}10^{-5} \neq 3\text{x}10^{-4}$$

TOT*H *equation:

$$3\left[\mathrm{H_3PO_4}\right]_{eq} + 2\left[\mathrm{H_2PO_4^-}\right]_{eq} + \left[\mathrm{HPO_4^{2-}}\right]_{eq} + \left[\mathrm{H^+}\right]_{eq} - \left[\mathrm{OH^-}\right]_{eq} = 9.34\text{x}10^{-5} \neq 9\text{x}10^{-4}$$