Numerical Solution of Acid/Base Problems

Example: How much NaOH must be added to a solution of 0.01 *M* Na_2HPO_4 + 0.003 *M* H_3PO_4 to increase the pH to 10.0, assuming all γ_i are 1.0?

- Species: ??
- Equilibrium constants
  - (*a*) ??
  - (*b*) ??
  - (*c*) ??
  - (*d*) ??
- Mass balances: ??
- Charge balance: ??

Numerical Solution of Acid/Base Problems

Example: NaOH required to adjust 0.01 *M* Na_2HPO_4 + 0.003 *M* H_3PO_4 to pH 10.0

- Species: H^+, OH^-, H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, Na^+
- Equilibrium constants
  - (*a*) $K_w = 10^{-14.0}$
  - (*b*) $K_{a1} = 10^{-2.2}$, $K_{a2} = 10^{-7.2}$, $K_{a3} = 10^{-12.2}$
  - (*c*) N/A
  - (*d*) None
- Mass balances: $TOTPO_4=0.013=10^{-1.89}$, $TOTNa=??$
- Charge balance:

$$[Na^+] + [H^+] = [OH^-] + [H_2PO_4^-] + 2[HPO_4^{2-}] + 3[PO_4^{3-}]$$

Numerical Solution of Acid/Base Problems

$$TOT\text{Na} + \left[\text{H}^+\right] = \frac{K_w}{\left[\text{H}^+\right]} + \alpha_1\left(TOT\text{PO}_4\right) + 2\alpha_2\left(TOT\text{PO}_4\right) + 3\alpha_3\left(TOT\text{PO}_4\right)$$

$$TOT\text{Na} = 2[\text{Na}_2\text{HPO}_4]_{\text{added}} + [\text{NaOH}]_{\text{added}} = [\text{Na}]_{\text{init}} + [\text{NaOH}]_{\text{added}}$$

pH	Na (init)	H	OH	H2PO4	HPO4	PO4	Sum (+)	Sum (-)	Net charge
10	2.00E-02	1.00E-10	1.00E-04	2.04E-05	1.29E-02	8.14E-05	2.00E-02	2.62E-02	-6.16E-03

The net charge must be zero, and the only term missing from the CB is $[NaOH]_{added}$, so that term must be 6.16E–3 *M*.

Note: If we had not assumed ideal behavior of solutes, the ***mass and charge balances*** would be based on ***concentrations***, whereas the ***equilibrium relationships*** would be based on ***activities***.

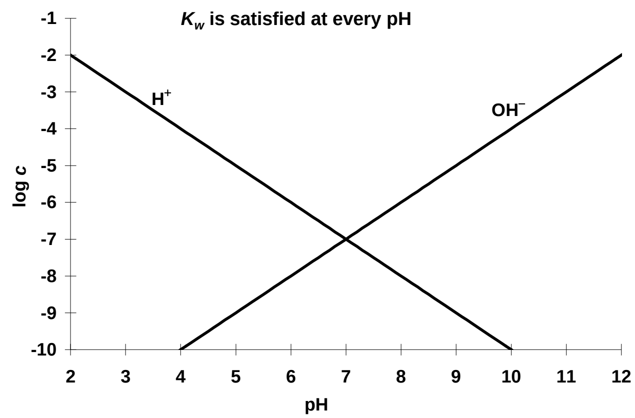
Graphical Solution of Acid/Base Problems

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

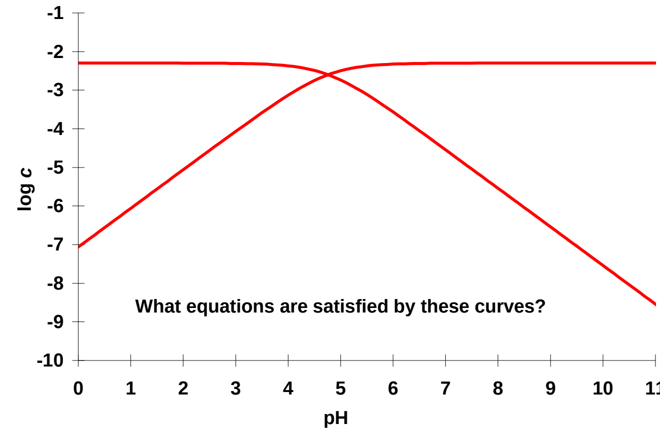
- Species: H^+, OH^-, H_2SO_3, HSO_3^-, SO_3^{2-}, HAc, Ac^-
- Equilibrium constants
  - (*a*) $K_w = 10^{-14.0}$
  - (*b*) $K_{a1,S} = 10^{-1.86}$, $K_{a2,S} = 10^{-7.30}$, $K_{a,Ac} = 10^{-4.76}$
  - (*c*) N/A
  - (*d*) None
- Mass balances: $TOTSO_3=10^{-4.0}$, $TOTAc=10^{-2.3}$
- Charge balance:

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

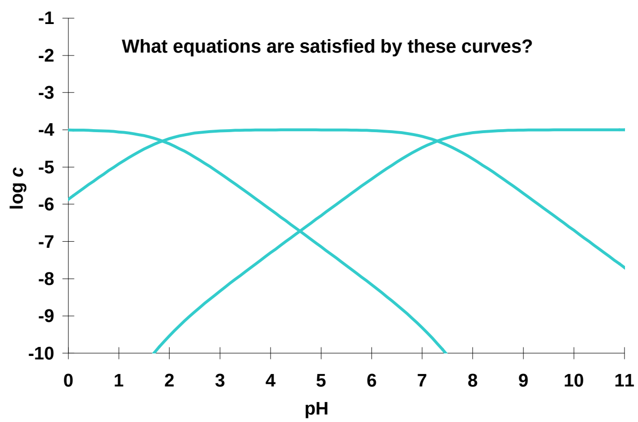
Graphical Solution of Acid/Base Problems



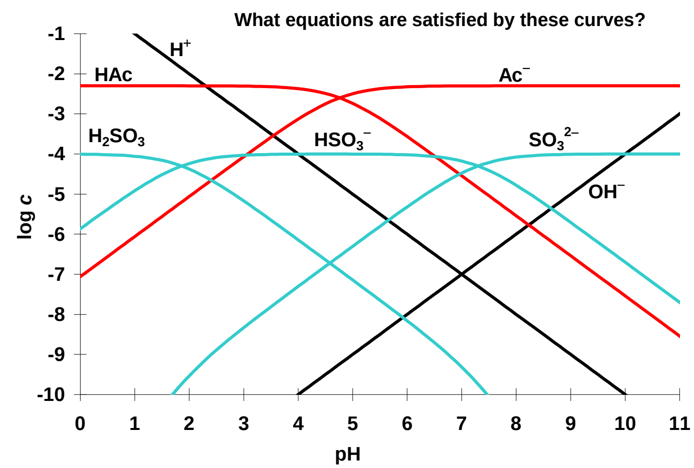
Graphical Solution of Acid/Base Problems



Graphical Solution of Acid/Base Problems



Graphical Solution of Acid/Base Problems



Graphical Solution of Acid/Base Problems

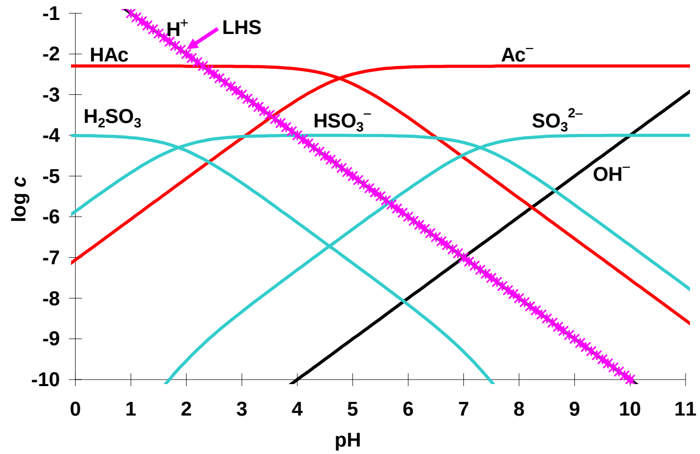
Example: Speciation of $10^{-4.0}$ *M* H_2SO_3 + $10^{-2.3}$ *M* HAc

- Species: H^+, OH^-, H_2SO_3, HSO_3^-, SO_3^{2-}, HAc, Ac^-
- 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: $TOTSO_3 = 10^{-4.0}$, $TOTAc = 10^{-2.3}$
- Charge balance:

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

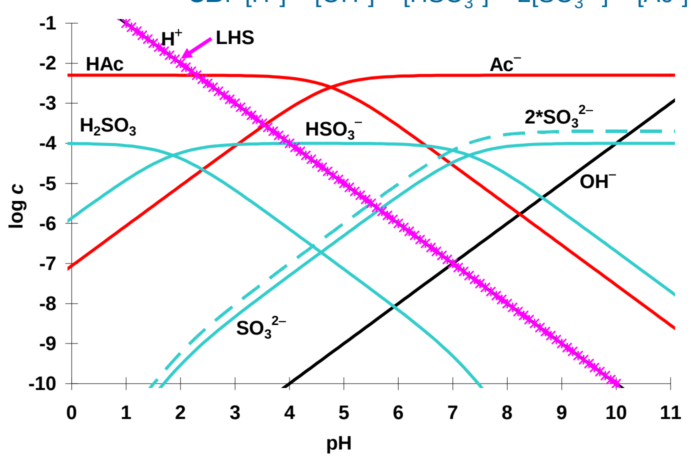
Graphical Solution of Acid/Base Problems

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



Graphical Solution of Acid/Base Problems

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



Graphical Solution of Acid/Base Problems