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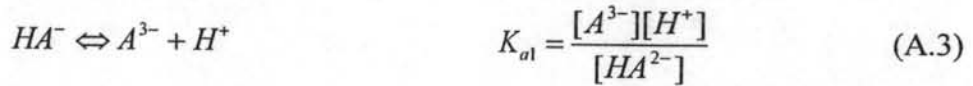
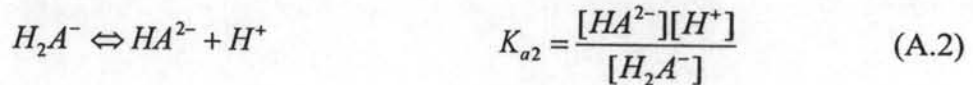
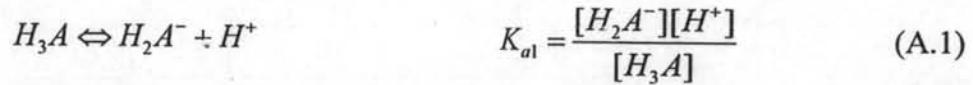
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APPENDICES

Appendix A Calculation Method for Deprotonation Curve of Polyprotic Acid

In this calculation citric acid is the representative of the polyprotic acid which is three steps depend upon the number of ionizable protons containing in the molecular as shown below



Rearrange K_a

$$\frac{K_{a1}[H_3A]}{[H^+]} = [H_2A^-] \qquad (A.4)$$

$$\frac{K_{a2}[H_2A^-]}{[H^+]} = [HA^{2-}] \qquad (A.5)$$

$$\frac{K_{a1}[HA^{2-}]}{[H^+]} = [A^{3-}] \qquad (A.6)$$

From the equilibrium reaction indicating the several deprotonation steps of acid, the concentration of each deprotonated species can be expressed as

$$[H_2A^-] = \frac{K_{a1}[H_3A]}{[H^+]} \qquad (A.4)$$

$$[HA^{2-}] = \frac{K_{a2}K_{a1}[H_3A]}{[H^+]^2} \qquad (A.7)$$

$$[A^{3-}] = \frac{K_{a3}K_{a2}K_{a1}[H_3A]}{[H^+]^3} \qquad (A.8)$$

The total citric acid concentration is the summation of all citric acid species

$$C_{total} = [H_3A] + [H_2A^-] + [HA^{2-}] + [A^{3-}] \quad (A.9)$$

This, in turn, means that there are *four* terms, α through α_3 , corresponding to the fractions of H_3A , ..., A^{3-} respectively

$$\alpha_0 = \frac{1}{1 + \frac{K_{a1}}{[H^+]} + \frac{K_{a1}K_{a2}}{[H^+]^2} + \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3}} \quad (A.10)$$

$$\alpha_1 = \frac{K_{a1}}{[H^+]} \alpha_0 \quad (A.11)$$

$$\alpha_2 = \frac{K_{a1}K_{a2}}{[H^+]^2} \alpha_0 \quad (A.12)$$

$$\alpha_3 = \frac{K_{a1}K_{a2}K_{a3}}{[H^+]^3} \alpha_0 \quad (A.13)$$

for the general fraction of polyprotic acid

$$\alpha_n = \frac{K_{a1}K_{a2}K_{a3}\dots K_{an}}{[H^+]^n} \alpha_0 \quad (A.14)$$

Equation A.10 Through A.14 may be used to construct the dissociation and composition-pH diagram for a polyprotic acid. The dissociation constants for this acid are not greatly different. With the result that in the intermediate pH region there is not a single dominant species. In fact, neither H_2A^- nor HA^{2-} exceed 80% of the total concentration at any point, and there is a significant pH range over which both these species co-exist in reasonable concentration.

Appendix B Order of Magnitude Mass Transfer Calculation

B.1. External Mass Transport

As verification of the mass transfer limitation of analcime dissolution, order of magnitude calculation may be performed to estimate the mass transfer rate in solution, which can then be compared to the measured dissolution rate. If the mass transfer of H^+ to an analcime particle is limiting, then the molar flux,

$$N_{H^+} = k_c ([H^+]_{Bulk} - [H^+]_{Surface}) = k_c [H^+]_{Bulk} \quad (B.1)$$

Where k_c is the mass transfer coefficient, which may be conservatively estimated by

$$k_c = \frac{ShD}{D_p} \quad (B.2)$$

The Sherwood number for flow around spherical particles dispersed in a batch reactor is estimated from

$$Sh = 2 + 0.6Re^{0.5} Sc^{0.33} \quad (B.3)$$

The smallest Sherwood number ($Sh=2$), the limiting case, yields the smallest mass transfer coefficient, k_c , which constrains the mass transfer rate to the minimum value for mass transfer limitations to exist. Therefore, the molar flux, of mass transfer rate, of H^+ to the external surface of analcime particle can be expressed as

$$N_{H^+} = k_c [H^+]_{Bulk} = \frac{2D}{D_p} [H^+]_{Bulk} \quad (B.4)$$

In aqueous systems, the diffusivity of a small molecule is on the order of 10^{-5} to 10^{-6} cm^2/s . The mean particle size, D_p , for the polydisperse system of dissolving

analcime particles can be measured using particle size distribution analyzer from Hartman (2005) works. The calculated mass transfer coefficient and corresponding mass transfer rate are shown in table B. 1 for analcime at 25 °C which exhibited the highest measured dissolution rate.

The stoichiometric coefficient, 4, can be used to compare the measured the dissolution rate to the mass transfer rate. The dissolution rate expressed in term of moles H^+ reacted per surface of analcime exposed per unit time is estimated by

$$r_{H^+}'' = n(r_{Al,O}'') \quad (B.5)$$

The dissolution rate is conservative estimated by assuming that only external analcime surfaces are accessible to H^+ attack, which results in the highest calculated values for comparison with the mass transfer rate, One readily observed in table C.1 that in all case the mass transfer rate was at least 2 orders of magnitude greater than the observed dissolution rate, demonstrating conclusively that analcime dissolution is reaction rate limited.

Table B.1 External mass transfer rate compared to measured dissolution rates

Conc. (mol/dm ³)	D _p (uM)	k _c (cm/min)	N _{H+} (mol/cm ² /min)	r _{H+} (mol/cm ² /min)
0.10	20.6	0.058	5.90E-06	8.14E-08
0.25	20.6	0.058	1.46E-05	1.60E-07
0.50	20.6	0.058	2.92E-05	3.15E-07
1.00	20.6	0.058	5.84E-05	5.53E-07
2.00	20.6	0.058	1.17E-04	7.34E-07
4.00	20.6	0.058	2.33E-04	8.83E-07
6.00	20.6	0.058	3.50E-04	9.43E-07
8.00	20.6	0.058	4.66E-04	1.03E-06

External surface for calculation equal to 0.68 m²/g (Hartman et, al 2005)

B.2 Internal Mass Transport

The Weisz-Prater Criterion uses measured values of the rate reaction, r_A' (obs) to determine if internal diffusion is limiting the reaction. From Internal effectiveness factor for a first-order in a spherical catalyst pellet,

$$\eta\phi_1^2 = 3(\phi_1 \coth \phi_1 - 1) \quad (\text{B.6})$$

The left-hand side is the Weisz-Prater parameter.

$$C_{WP} = \eta\phi_1^2 \quad (\text{B.7})$$

$$\begin{aligned} &= \frac{\text{observed (actual) reaction rate}}{\text{reaction rate evaluated at } C_{AS}} * \frac{\text{reaction rate evaluated at } C_{AS}}{\text{a diffusion rate}} \\ &= \frac{\text{actual reaction rate}}{\text{a diffusion rate}} \end{aligned}$$

Substituting for

$$\eta = \frac{-r_A'(obs)}{-r_{As}'} \quad \text{and} \quad \phi_1^2 = \frac{-r_{As}'' S_a \rho_c R^2}{D_e C_{As}} = \frac{-r_{As}' \rho_c R^2}{D_e C_{As}} \quad (\text{B.8})$$

From previous equation we have

$$C_{WP} = \frac{-r_A'(obs)}{-r_{As}'} \left(\frac{-r_{As}' \rho_c R^2}{D_e C_{As}} \right) \quad (\text{B.9})$$

$$C_{WP} = \eta\phi_1^2 = \frac{-r_A'(obs) \rho_c R^2}{D_e C_{As}} \quad (\text{B.10})$$

All the term are either measures or known. Consequently, we can calculate C_{WP} . If $C_{WP} \ll 1$ There are no diffusion limitations and consequently no concentration

gradient exists within the pellet. If $C_{wp} \gg 1$ internal diffusion limits the reaction severely.

Table B.2 Dissolution rate of analcime at the different size of particle at 25 °C

Conc. (M)	Pellet Radius 1.19 mm**		Pellet radius 38*10 ⁻³ mm		C _{WP}	
	Si (mmol/g.min)	Al (mmol/g.min)	Si (mmol/g.min)	Al (mmol/g.min)	Si	Al
0.25	0.0126	0.0066	0.5039	0.2733	9.17E-04	9.16E-04
1	0.062	0.0275	1.7864	0.9403	9.22E-04	9.19E-04
2	0.104	0.0546	2.0572	1.2483	9.30E-04	9.27E-04
4	0.166	0.0866	2.6172	1.5004	9.37E-04	9.34E-04

**Data from Wattanaparadorn (2002)

Form The Weisz-Prater Criterion

$$\frac{-r'_A(obs)R^2\rho_c}{D_e C_{As}} = \eta\phi_1^2 = 3(\phi_1 \coth \phi_1 - 1) \quad (B.11)$$

Letting the subscripts 1 and 2 refer to run 1 and 2, we apply this to run 1 and 2 and then take the ratio to obtain

$$\frac{-r'_{A2}R_2^2}{-r'_{A1}R_1^2} = \frac{\phi_{12} \coth \phi_{12} - 1}{\phi_{11} \coth \phi_{11} - 1} \quad (B.12)$$

The terms ρ_c , D_e and C_{As} cancel because the runs were carried out under identical conditions. The Thiele modulus is

$$\phi_1 = R \sqrt{\frac{-r'_{As}\rho_c}{D_e C_{As}}} \quad (B.13)$$

taking the ratio of the Thiele modulus for aluminum at the concentration of 0.25 M

$$\phi_{11} = \frac{R_1}{R_2} \phi_{12} = \frac{1.19 * 10^{-3} m}{38 * 10^{-6} m} \phi_{12} = 31.3158 \phi_{12} \quad (\text{B.14})$$

Substituting for ϕ_{11} in the equation B.12 and evaluating $-r_A$ and R give us

$$\left(\frac{0.2733}{0.0066} \right) * \left(\frac{38 * 10^{-6}}{1.19 * 10^{-3}} \right)^2 = \frac{\phi_{12} \coth \phi_{12} - 1}{31.3158 \phi_{12} \coth(31.3158) \phi_{12} - 1} \quad (\text{B.15})$$

$$0.0422 = \frac{\phi_{12} \coth \phi_{12} - 1}{31.3158 \phi_{12} \coth(31.3158) \phi_{12} - 1}$$

We have one equation and one unknown. By solving this equation, we find that

$$\phi_{12} = 0.0303 \text{ for } R_2 = 38 * 10^{-6} m$$

$$\phi_{11} = 0.9489 \text{ for } R_2 = 1.19 * 10^{-3} m$$

The corresponding effectiveness factor are

$$\eta_2 = \frac{3(\phi_{12} \coth \phi_{12} - 1)}{\phi_{12}^2} = \frac{3(0.0303 \coth 0.0303 - 1)}{(0.0303)^2} = 0.9999$$

next we find the Weisz-Prater parameter.

$$C_{wp} = \eta \phi_1^2 = 0.9999 * (0.0303)^2 = 9.16 * 10^{-4}$$

The Weisz-Prater parameter were calculated and shown in table B.2. One observed from the table is The Weisz-Prater parameter are much less than 1 in all cases so I can say that my systems are in reaction-limited regimes.

Appendix C Experimental Data

1 Analcime Composition Analyzed

Table C.1 Analcime Composition Analyzed by AAS

Sample No.	mol%			Molar Ratio		
	Al	Si	Na	Al	Si	Na
1	28.07	63.00	8.94	1.00	2.24	0.32
2	28.19	62.06	9.76	1.00	2.20	0.35
3	28.16	62.19	9.66	1.00	2.21	0.34
4	27.26	63.58	9.17	1.00	2.33	0.34
Avg	27.92	62.70	9.38	1.00	2.25	0.34
Std.	0.44	0.72	0.39	0.00	0.06	0.01

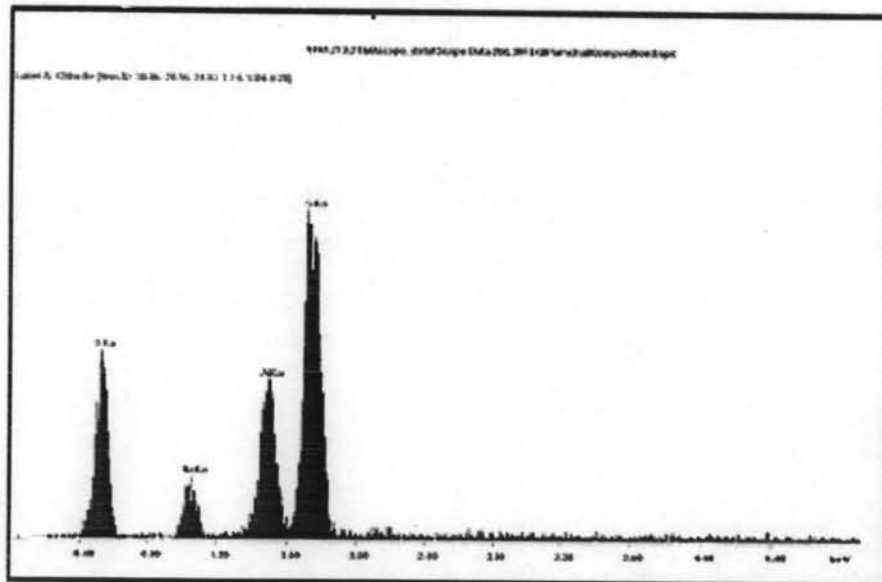


Figure C.1 Analcime composition analyzed by EDX

2. Analcime Dissolution Rate in Citric Acid

Table C.2 Analcime Dissolution Rate in Citric Acid at 5 °C

Citric acid concentration (mol/L)	$-r_{Si}$ (mmol/g.min)	$-r_{Al}$ (mmol/g.min)	$-r_{Si} / -r_{Al}$
0.25	0.1247	0.0825	1.5111
0.75	0.1877	0.1268	1.4802
1.50	0.2646	0.1652	1.6015
3.00	0.2820	0.1776	1.5883

Table C.3 Analcime Dissolution Rate in 0.5 M HCl/Citric acid at 25 °C

Citric acid Concentration (mol/L)	$-r_{Si}$ (mmol/g.min)	$-r_{Al}$ (mmol/g.min)	$-r_{Si} / -r_{Al}$
0.00	1.0203	0.5353	1.9060
0.10	1.1438	0.6023	1.8991
0.25	1.2657	0.7050	1.7952
0.50	1.4601	0.8606	1.6966
0.75	1.5208	0.8631	1.7619
1.50	1.7870	1.0097	1.7698
3.00	1.8388	1.0754	1.7099

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