p. 492 … two velocity terms, … for the air boundary layer $v_a = (D_a K'_H) / z_a$

p. 492 ANSWER: $E_{theor} = v_w = D_f / z_w = $ 1577 m/yr.

p. 156 $-\mathrm{d}m_{Fe^{2+}} / \mathrm{d}t = 8 \times 10^{13} \times 10^{-3} \times (10^{-9})^2 \times 0.2 = 1.6 \times 10^{-8}$ mol/L/min

p. 157 Thus, $t_{1/2} = \ln(1/2)/{-}1.6 \times 10^{-5} = 43321$ min or 722 hr.

QUESTIONS:
ANSWER: 722 hr
ANSWER: 4.3 minutes

p. 290 $$\mathrm{d}\psi / \mathrm{d}x = \sqrt{(8(RT/\varepsilon)m_{i,\infty})} \sinh(+F\psi / 2RT) \qquad (6.57)$$
where $b = + F / (2RT)$ and …

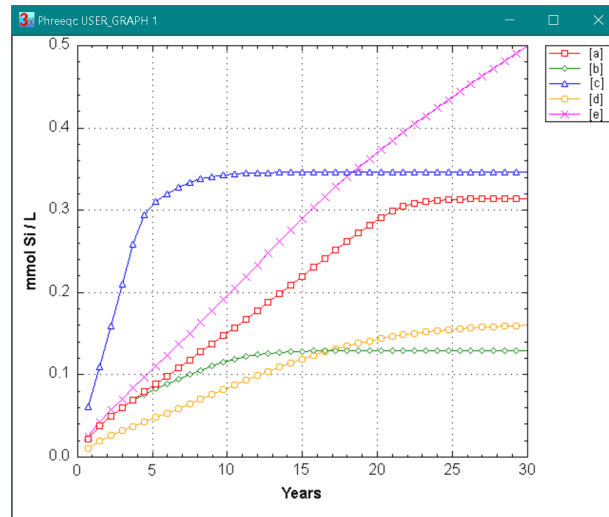Figure 8.18 should be, with the time for K-feldspar dissolution increased to 30 years:

Figure 8.18. PHREEQC calculation of K-feldspar dissolution kinetics using Equation (8.26). The conditions are varied as follows: **(a)** Equilibrium for gibbsite imposed, initial pH = 4 and 10°C. **(b)** as case (a) but without equilibrium for gibbsite, **(c)** as case (a) but using a temperature of 25°C, **(d)** as case (a) but with an initial pH of 5, **(e)** as case (a) but with $P_{CO_2} = 10^{-2.5}$ atm imposed.

In the 10th printing (in 2013) of Appelo and Postma, 2005, we define the pore water diffusion coefficient D_p for calculating diffusion in a porous medium. In previous printings, this was called the effective diffusion coefficient D_e. The change in nominology is in line with current terminology.
In short:
D_f is the diffusion coefficient in "free" water (m^2/s).
The pore water diffusion coefficient is:
$$D_p = \frac{D_f}{\theta^2} \qquad (3.44)$$
where θ is the tortuosity of the porous medium (no dimension).
The effective diffusion coefficient is:

1

$$D_e = \varepsilon_w D_p = \frac{\varepsilon_w D_f}{\theta^2} \tag{3.45}$$

D_p is for calculating concentration changes in a porous medium (with the same formulas as used for "free" water if the porosity ε_w is the same throughout).
D_e is for calculating the flux (mol/m²/s).

Errata in printings before 2013.

p. 264   Percolation gives 0.015 m/yr $\times$ 1 $\times$ 1 m^2 = 0.015m^3/yr.

p. 337   EXAMPLE 7.6. *Calculate the surface potential for 2.6×10^{-7} eq/m^2*

p. 630
9.1. Find H$_2$AsO$_4^-$ = 0.42×As(5) = 0.49 μM with the speciation factor. Using Equation (9.32), pe = 0.041, Eh = 0.024V.

p. 548

$$... \quad = \quad A$$

$$... \quad = \begin{bmatrix} 1 & 0 & 0 & 0 \\ =4 & 7 & -2 & 0 \\ 0 & -2 & 5 & -2 \\ 0 & 0 & -2 & 3 \end{bmatrix} \tag{11.22}$$

Errata in printings before 2008.

p. 64   ANSWER: Hence v_{H_2O} = 0.1 / 0.022 = 4.6 mm/yr. Age: 3000 mm / 4.6 mm/yr = 652 yr.

p. 82   ANSWER: 5.9 in case dispersion is absent.

p. 222

$$\delta^{13}C = \frac{\delta^{13}C_i \times TIC_i + \delta^{13}C_{dol} \times 2 \times D_{dol} - (\delta^{13}C + \varepsilon_{cc/sol}) P_{cc}}{TIC_i + 2 \times D_{dol} - P_{cc}} \tag{5.52}$$

p. 249
structure of the crystal. The substitution of Si^{4+} by Al^{3+} reduces the positive charge by one in an

p. 269

$$\frac{[Na^+]}{\sqrt{[Ca^{2+}]}} = K_{Ca\backslash Na} \frac{[Na\text{-}X]}{\sqrt{[Ca\text{-}X_2]}}$$

p. 270
Equation (6.33) we can calculate that f = 0.43, c_{Na^+} = 0.7 meq/L and $c_{Ca^{2+} + Mg^{2+}}$ = 1.08 meq/L in the

p. 290

2

where $b = -F / (2RT)$ and $a = \sqrt{8(RT / \varepsilon)m_{i,\infty}}$.

$$\sigma_{DL} = \sqrt{8\varepsilon RT m_{i,\infty}} \sinh(F\psi_0 / 2RT) \tag{6.62}$$

7.19. Estimate the percentage Ni^{2+} at trace (10^{-8} M) concentration sorbed on smectite in 3.3 mM Ca^{2+} solution, 1 g smectite/L, $CEC = 0.87$ meq/g. Compare with Figure 7.18, pH < 5. Note to include NiX_2 (cf. Table 6.4).
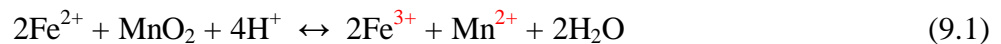   b. Include 1.86 mg ferrihydrite, vary log_k for sorption of Ni^{2+} on the strong sites?

weathering rates k_i at another temperature (T, K) than 8°C (281 K):
In Equation (8.27) replace 271 by 281

$$2Fe^{2+} + MnO_2 + 4H^+ \leftrightarrow 2Fe^{3+} + Mn^{2+} + 2H_2O \tag{9.1}$$

ANSWER: pe = -pH - ½log[P_{H_2}], pe = -pH + 2.5

New **WATEQ4F** database speciates As differently (p. 425-428): download *As_p425.pdf* (32 kB). Or download the PHREEQC input file *Table9_3* with the log K numbers from Table 9.3.

ANSWER: 0.0073 m^2/mol pyrite (valid for 2 cm crystals).

$$c'_w = \frac{(D_a / z_a)c_a + (D_f / z_w)c_w}{K'_H D_a / z_a + D_f / z_w} \tag{10.6}$$

where D_e is the diffusion coefficient in the stagnant region, a is the size (m), and $f_{s\rightarrow1}$ is a
…
and $\rho_b/\varepsilon = 6$ kg/L. The diffusion coefficient is $D_e = 0.99\times10^{-10}$ m^2/s in the clay.
[*Note:* the pore water diffusion coefficient D_p is used since the 10th printing]

… The exchange factor $\alpha = 0.99\times10^{-10} \times$ 0.12 / $(0.165 \times 0.53)^2 = 1.55\times10^{-9}$/s.

is changed to: 20 graph_y log(tot("Phenol") * 94e3).

In Equations (11.3) and (11.4), change $(c_0 + c_i)$ to $(c_0 - c_i)$

5.2. pH = 6.81, $[CO_3^{2-}]$ = $10^{-6.38}$; pH = 9.95, $[CO_3^{2-}]$ = 0.4 mM (without the contribution of OH⁻ to *Alk*), or pH = 9.86, $[CO_3^{2-}]$ = 0.33 mM (when including the contribution of OH⁻ to *Alk*).

5.5. Ca^{2+} = 1.58 mmol/L (with K_{cc} = $10^{-8.3}$), Ca^{2+} = 1.38 mmol/L (with K_{cc} = $10^{-8.5}$).

5.6. P_{CO_2} = 0.02 atm (with K_{cc} = $10^{-8.3}$), 0.03 atm (with K_{cc} = $10^{-8.5}$).

5.7. P_{CO_2} = $10^{-2.55}$ atm (with K_{cc} = $10^{-8.3}$), $10^{-2.45}$ atm (with K_{cc} = $10^{-8.5}$).

6.7d. …. 26.9 pore volumes = 7935 m³ water.

9.3. Note that $Pb(OH)_3^-$ is dominant for pH > 9.4, as will become evident when eqns 3) and 4) are combined.