

TITLE Example 9.--Kinetically controlled oxidation of ferrous iron. Decoupled valence states of iron.

SOLUTION\_MASTER\_SPECIES

Fe_di	Fe_di+2	0.0	Fe_di	55.847
Fe_tri	Fe_tri+3	0.0	Fe_tri	55.847

SOLUTION\_SPECIES

Fe\_di+2 = Fe\_di+2  
log\_k 0.0

Fe\_tri+3 = Fe\_tri+3  
log\_k 0.0

#  
# Fe+2 species  
#  
Fe\_di+2 + H2O = Fe\_diOH+ + H+  
log\_k -9.5  
delta\_h 13.20 kcal

#  
#... and also other Fe+2 species  
#  
Fe\_di+2 + Cl- = Fe\_diCl+  
log\_k 0.14

Fe\_di+2 + CO3-2 = Fe\_diCO3  
log\_k 4.38

Fe\_di+2 + HCO3- = Fe\_diHCO3+  
log\_k 2.0

Fe\_di+2 + SO4-2 = Fe\_diSO4  
log\_k 2.25  
delta\_h 3.230 kcal

Fe\_di+2 + HSO4- = Fe\_diHSO4+  
log\_k 1.08

Fe\_di+2 + 2HS- = Fe\_di(HS)2  
log\_k 8.95

Fe\_di+2 + 3HS- = Fe\_di(HS)3-  
log\_k 10.987

Fe\_di+2 + HPO4-2 = Fe\_diHPO4  
log\_k 3.6

Fe\_di+2 + H2PO4- = Fe\_diH2PO4+  
log\_k 2.7

Fe\_di+2 + F- = Fe\_diF+  
log\_k 1.0

#  
# Fe+3 species  
#  
Fe\_tri+3 + H2O = Fe\_trioOH+2 + H+  
log\_k -2.19  
delta\_h 10.4 kcal

#  
#... and also other Fe+3 species  
#  
Fe\_tri+3 + 2 H2O = Fe\_tri(OH)2+ + 2 H+  
log\_k -5.67  
delta\_h 17.1 kcal

Fe\_tri+3 + 3 H2O = Fe\_tri(OH)3 + 3 H+  
log\_k -12.56  
delta\_h 24.8 kcal

Fe\_tri+3 + 4 H2O = Fe\_tri(OH)4- + 4 H+  
log\_k -21.6  
delta\_h 31.9 kcal

2 Fe\_tri+3 + 2 H2O = Fe\_trii(OH)2+4 + 2 H+  
log\_k -2.95  
delta\_h 13.5 kcal

3 Fe\_tri+3 + 4 H2O = Fe\_trii(OH)4+5 + 4 H+  
log\_k -6.3  
delta\_h 14.3 kcal

Fe\_tri+3 + Cl- = Fe\_tricl+2  
log\_k 1.48

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delta_h 5.6      kcal
Fe_tri+3 + 2 Cl- = Fe_tricl2+
log_k 2.13
Fe_tri+3 + 3 Cl- = Fe_tricl3
log_k 1.13
Fe_tri+3 + SO4-2 = Fe_triso4+
log_k 4.04
delta_h 3.91      kcal
Fe_tri+3 + HSO4- = Fe_trihso4+2
log_k 2.48
Fe_tri+3 + 2 SO4-2 = Fe_tri(SO4)2-
log_k 5.38
delta_h 4.60      kcal
Fe_tri+3 + HPO4-2 = Fe_trihpo4+
log_k 5.43
delta_h 5.76      kcal
Fe_tri+3 + H2PO4- = Fe_trih2po4+2
log_k 5.43
Fe_tri+3 + F- = Fe_trif+2
log_k 6.2
delta_h 2.7      kcal
Fe_tri+3 + 2 F- = Fe_trif2+
log_k 10.8
delta_h 4.8      kcal
Fe_tri+3 + 3 F- = Fe_trif3
log_k 14.0
delta_h 5.4      kcal
PHASES
Goethite
    Fe_triooh + 3 H+ = Fe_tri+3 + 2 H2O
    log_k -1.0
END
SOLUTION 1
    pH 7.0
    pe 10.0 O2(g) -0.67
    Fe_di 0.1
    Na 10.
    Cl 10. charge
EQUILIBRIUM_PHASES 1
    O2(g)           -0.67
RATES
Fe_di_ox
    -start
    10 Fe_di = TOT("Fe_di")
    20 if (Fe_di <= 0) then goto 200
    30 p_o2 = SR("O2(g)")
    40 moles = (2.91e-9 + 1.33e12 * (ACT("OH-"))^2 * p_o2) * Fe_di * TIME
    200 SAVE moles
    -end
KINETICS 1
Fe_di_ox
    -formula Fe_di -1.0 Fe_tri 1.0
    -steps 100 400 3100 10800 21600 5.04e4 8.64e4 1.728e5 1.728e5 1.728e5
    -step_divide 1e-4
INCREMENTALREACTIONS true
SELECTED_OUTPUT
    -file ex9.sel
    -reset false
USER_PUNCH
    -headings Days Fe(2) Fe(3) pH si_goethite
    10 PUNCH SIM_TIME / 3600 / 24, TOT("Fe_di")*1e6, TOT("Fe_tri")*1e6, -LA("H+"), \
        SI("Goethite")
USER_GRAPH Example 9
    -headings time Fe(2) Fe(3) pH
    -chart_title "Oxidation of Ferrous Iron"
    -axis_titles "Time, in days" "Micromole per kilogram water" "pH"
    -axis_scale secondary_y_axis 4.0 7.0 1.0 0.5
    -start

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10 GRAPH_X TOTAL_TIME / 3600 / 24
20 GRAPH_Y TOT("Fe_di")*1e6, TOT("Fe_tri")*1e6
30 GRAPH_SY -LA("H+")
-end
END
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