

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

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_triOH+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_tri2(OH)2+4 + 2 H+
log_k -2.95
delta_h 13.5 kcal

3 Fe_tri+3 + 4 H2O = Fe_tri3(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 1.728e5
-step_divide 1e-4
INCREMENTAL_REACTIONS 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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