Kimyasal Denge ve Mineral Çözünürlüğü

GEOCHEMISTRY, GROUNDWATER AND POLLUTION
SECOND EDITION

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law of mass action = kütle akısı yasası

$$aA + bB \leftrightarrow cC + dD$$

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$CaF_2 \leftrightarrow Ca^{2+} + 2F^-$$

$$K_{fluorite} = [Ca^{2+}][F^-]^2 = 10^{-10.57} \quad \text{at } 25°C$$

$$\log K_{fluorite} = \log[Ca^{2+}] + 2\log[F^-] = -10.57$$

Toplam konsantrasyon, Efektif, aktif (etkili) konsantrasyon

Table 4.1. Conventions for standard states and activities.

	Concentration measure	Symbol	Standard state
Gases	Gas pressure (atm)/1 atm	P_i / P^0	$P^0 = 1$ atm
Solid and liquid mixtures	Mole-fraction	χ	$\chi = 1$
Aqueous solutes	Molality/(1 molal)	m_i / m^0	$m^0 = 1$ mol/kg H_2O
Exchangeable ions	Equivalent- or Mole-fraction	β or β^M	$\beta = 1$, $\beta^M = 1$

Aktif konsantrasyon = aktivite katsayısı * toplam konsantrasyon

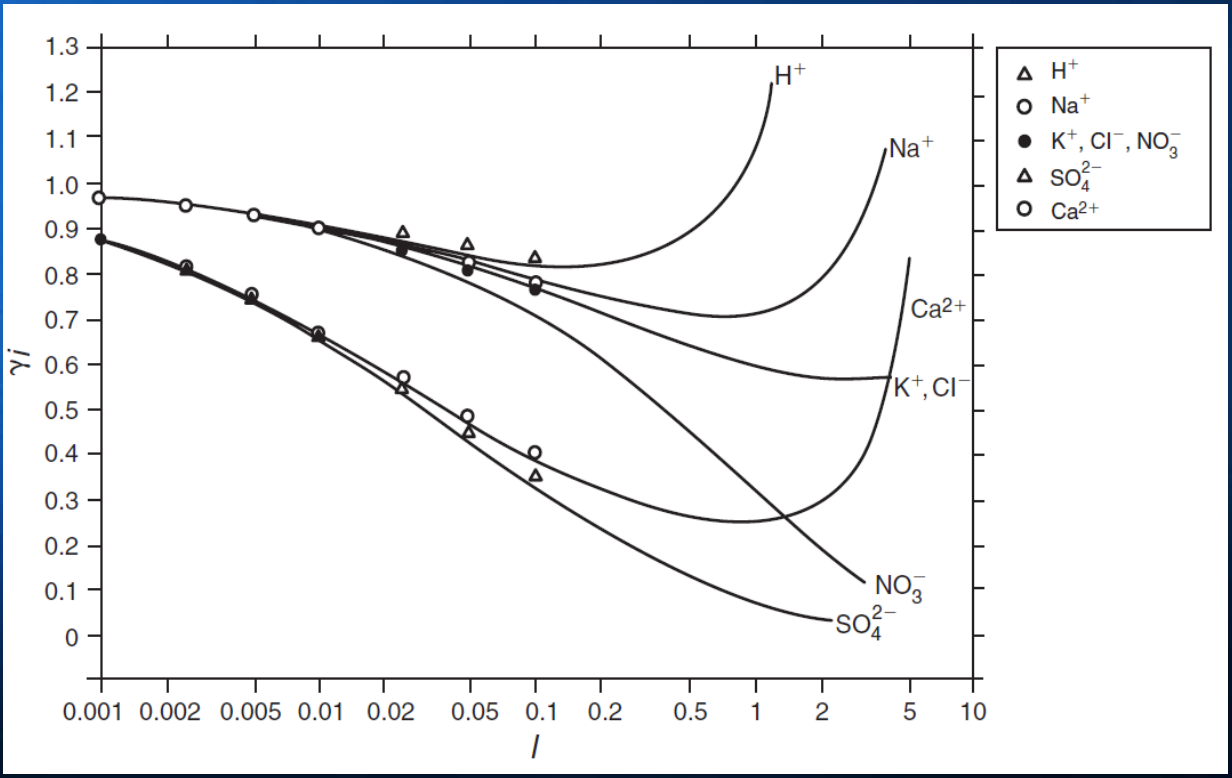
$$[i] = \gamma_i \cdot m_i / m_i^0 \equiv \gamma_i \cdot m_i$$

İyonik güç: iyon toplam konsantrasyonları ile yüklerinin çarpımının toplamının yarısı ☺

$$I = ½ \sum (m_i / m_i^0 \cdot z_i^2) \equiv ½ \sum m_i \cdot z_i^2$$

İyonik Güç eşitliği

$$\log \gamma_i = -Az_i^2\left(\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right)$$



Doygunluk İndisi ve Gibbs Serbest Enerjisi

$$\Omega = IAP/K$$

$$SI = \log(IAP/K)$$

calculation of mass action constants

$$aA + bB \leftrightarrow cC + dD$$

$$\Delta G_r^0 = -RT \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$\Delta G_r^0 = -RT \ln K$$

$$\Delta G_r^0 = \sum \Delta G_{f\ products}^0 - \sum \Delta G_{f\ reactants}^0$$

$\Delta G_r > 0$ the reaction proceeds to the left;
$\Delta G_r = 0$ the reaction is at equilibrium;
$\Delta G_r < 0$ the reaction proceeds to the right.

8.31410₃kJ/mol/deg

Kelvin °C 273

Örnek hesaplama (Gibbs serbest enerjisi)

EXAMPLE 4.4. *Calculation of solubility products from Gibbs free energy data*
Calculate the solubility product of calcite from the Gibbs free energies of formation at 25°C (Wagman et al., 1982):

$$\Delta G^0_{f\,CaCO_3} = -1128.8 \text{ kJ/mol}$$
$$\Delta G^0_{f\,Ca^{2+}} = -553.6 \text{ kJ/mol}$$
$$\Delta G^0_{f\,CO_3^{2-}} = -527.8 \text{ kJ/mol}$$

ANSWER:
For the reaction $CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$
we obtain

$$\Delta G^0_r = \Delta G^0_{f\,Ca^{2+}} + \Delta G^0_{f\,CO_3^{2-}} - \Delta G^0_{f\,CaCO_3}$$
$$\Delta G^0_r = -553.6 - 527.8 + 1128.8 = 47.4 \text{ kJ/mol}$$
$$\Delta G^0_r = -RT \ln K$$
$$47.4 = -8.314\times10^{-3} \times 298.15 \times 2.303 \log K = -5.708 \log K$$
$$\log K = 47.4/ -5.708 = -8.30$$

Calculation of mass action constants at different temperature

Örnek hesaplama Van't Hoff eşitliği

$$\log K_{T_1} - \log K_{T_2} = \frac{-\Delta H_r^0}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

EXAMPLE 4.5. *Temperature dependency of the solubility product*
Calculate the solubility product of calcite at 10°C from the following enthalphies of formation (Wagman et al., 1982):

$$\Delta H^0_{f\,CaCO_3} = -1206.9 \text{ kJ/mol}$$
$$\Delta H^0_{f\,Ca^{2+}} = -542.8 \text{ kJ/mol}$$
$$\Delta H^0_{f\,CO_3^{2-}} = -677.1 \text{ kJ/mol}$$

ANSWER:
For the reaction $CaCO_3 \leftrightarrow Ca^{2+} + CO_3^{2-}$
we may write,

$$\Delta H_r^0 = -542.8 + (-677.1) - (-1206.9) = -13.0 \text{ kJ/mol}$$

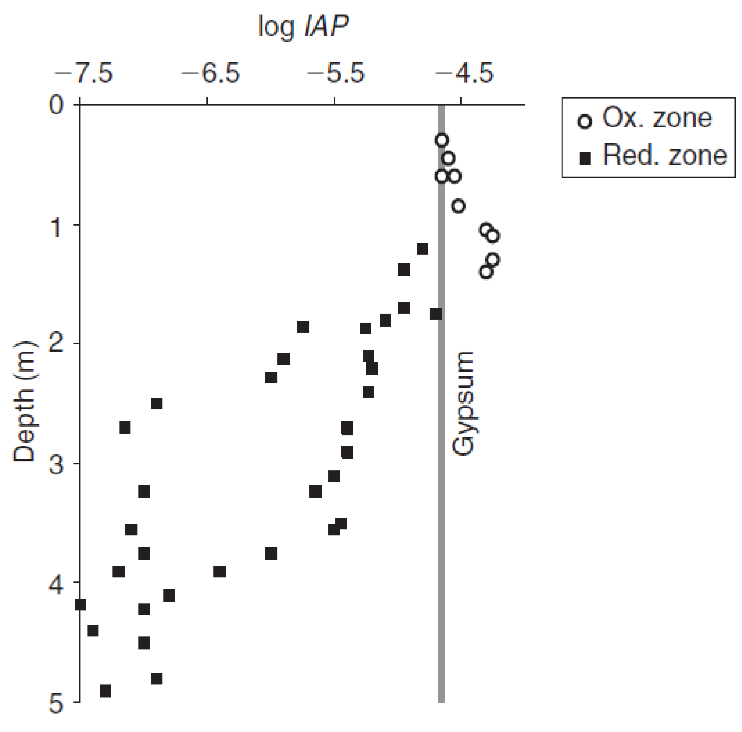
which means that the reaction is exothermal: the system heats up when calcite dissolves. The difference in $\log K$ between 25°C and 10°C, according to Equation (4.29) is:

$$\log K_{25} - \log K_{10} = \frac{-\Delta H_r^0}{2.303\,R}\left(\frac{1}{298.15} - \frac{1}{283.15}\right)$$
$$= \frac{-13.0}{2.303 \times 8.314\times10^{-3}}\left(\frac{1}{298.15} - \frac{1}{283.15}\right)$$
$$= -0.12$$

In EXAMPLE 4.4 it was calculated that $\log K_{calcite}$ at 25°C is −8.30, so that at 10°C $K_{calcite}$ = −8.30 + 0.12 = −8.18. Thus for an exothermal reaction the solubility increases with decreasing temperature and vice versa for an endothermal reaction.

Doygunluk İndisi

Örnek: Jips minerali



$$CaSO_4 \cdot 2H_2O \leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$

$$K = \frac{[Ca^{2+}][SO_4^{2-}][H_2O]^2}{[CaSO_4 \cdot 2H_2O]} = 10^{-4.6}$$

$$K_{gypsum} = [Ca^{2+}][SO_4^{2-}] = 10^{-4.60} \quad \text{at } 25°C$$

$$K_{gypsum} = [Ca^{2+}][SO_4^{2-}] \quad \text{(activities at equilibrium)}$$

$$IAP_{gypsum} = [Ca^{2+}][SO_4^{2-}] \quad \text{(activities in the water sample)}$$

$$SI = \log(IAP/K)$$

PhreeqC SI hesaplaması

Parkhurst, D.L., and Appelo, C.A.J., 2013, Description of input and examples for PHREEQC version 3—A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p., available only at http://pubs.usgs.gov/tm/06/a43/.

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-----------------------------Solution composition-------

   Elements               Molality           Moles

   Ca                     2.495e-04          2.495e-04
   F                      2.895e-04          2.895e-04

------------------------------Description of solution--


pH                                        =  7.000
pe                                        =  4.000
Activity of water                         =  1.000
Ionic strength                            =  6.427e-04
Mass of water (kg)                        =  1.000e+00
Total alkalinity (eq/kg)                  = -4.154e-08
Total carbon (mol/kg)                     =  0.000e+00
Total CO2 (mol/kg)                        =  0.000e+00
Temperature (deg C)                       = 25.000
Electrical balance (eq)                   =  2.095e-04
Percent error, 100*(Cat-|An|)/(Cat+|An|) = 26.61
                               Iterations = 3
Total H                                   =  1.110124e+02
Total O                                   =  5.550622e+01
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------------------------------Distribution of species-------------------------

                                                      Log        Log       Log
     Species       Molality       Activity        Molality   Activity    Gamma

     OH-           1.030e-07      1.001e-07        -6.987     -7.000    -0.012
     H+            1.028e-07      1.000e-07        -6.988     -7.000    -0.012
     H2O           5.551e+01      1.000e+00        -0.000     -0.000     0.000
Ca            2.495e-04
     Ca+2          2.489e-04      2.221e-04        -3.604     -3.653    -0.049
     CaF+          5.590e-07      5.431e-07        -6.253     -6.265    -0.012
     CaOH+         3.794e-10      3.687e-10        -9.421     -9.433    -0.012
F             2.895e-04
     F-            2.889e-04      2.807e-04        -3.539     -3.552    -0.012
     CaF+          5.590e-07      5.431e-07        -6.253     -6.265    -0.012
     HF            4.209e-08      4.210e-08        -7.376     -7.376     0.000
     HF2-          4.667e-11      4.534e-11       -10.331    -10.343    -0.012
     H2F2          4.618e-15      4.619e-15       -14.336    -14.335     0.000
H(0)          1.416e-25
     H2            7.078e-26      7.079e-26       -25.150    -25.150     0.000
O(0)          0.000e+00
     O2            0.000e+00      0.000e+00       -42.080    -42.080     0.000


------------------------------Saturation indices----------------------------


     Phase          SI       log IAP    log KT

     Fluorite      -0.16     -10.76     -10.60       CaF2
     H2(g)        -21.96     -22.00      -0.04       H2
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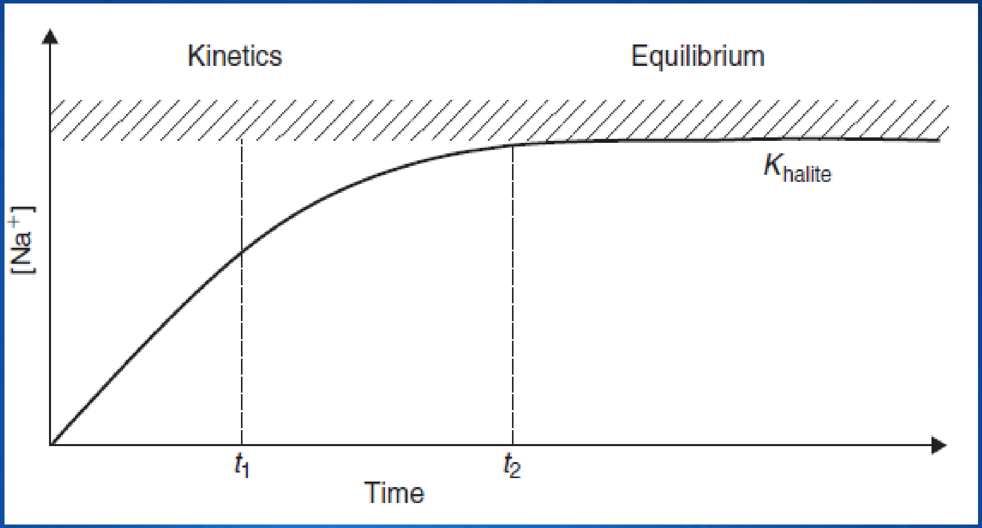
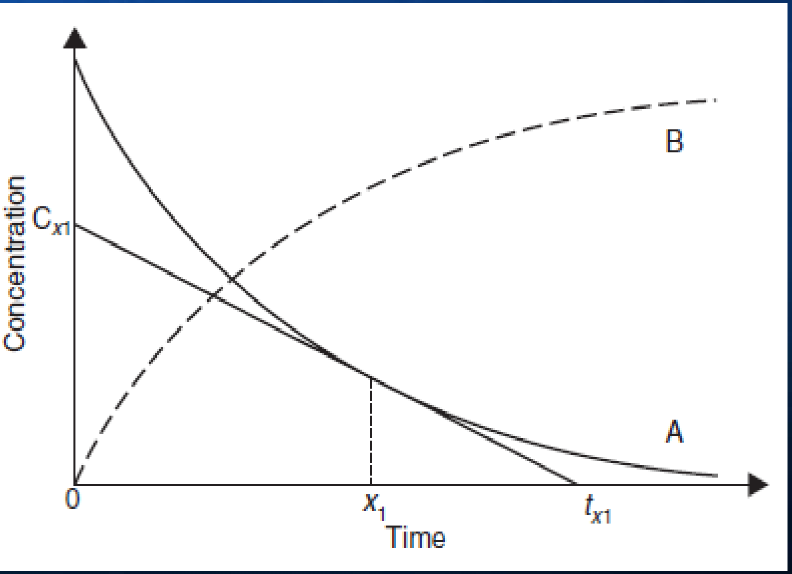
Kimyasal Kinetik – Kimyasal Denge



$$\text{rate} = -dc_A / dt = dc_B / dt$$



Reaksiyon kinetiği