P XXX/00 Terms and definitions used with Thermodyn

Free energy equation: $\Delta G_r = \Delta H_r - T \cdot \Delta S_r$

Equilibrium equation: $\Delta G_r = 0$

$\Delta G_r^0 = -R \cdot T \cdot \ln K^0$ $\qquad$ $\Delta G_r^0 = \sum_j v_j Gf_{P_j}^0 - \sum_i v_i Gf_{S_i}^0$ (2)

or

$$K^0 = \exp \left[\frac{-\Delta G_r^0}{R \cdot T} \right]$$

Disequilibrium equation: $\Delta G_r < 0$

$\Delta G_r = \Delta G_r^0 + R \cdot T \cdot \ln Q$ (3)

or

$\Delta G_r = R \cdot T \cdot \ln \frac{Q}{K^0}$ $\qquad$ $\frac{Q}{K^0} < 1$

or

$$Q = K^0 \cdot \exp \left[\frac{\Delta G_r}{R \cdot T} \right]$$

or

$$Q = K^0 \cdot \exp \left[\frac{-E \cdot n \cdot F}{R \cdot T} \right]$$

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Influence of temperature changes on equilibrium equation:

$$\Delta G^0_{r,T_{act}} = \Delta G^0_{r,T_{ref}} \cdot \frac{T_{act}}{T_{ref}} + \Delta H^0_{r,T_{ref}} \cdot \frac{T_{ref} - T_{act}}{T_{ref}}$$

Influence of temperature changes on equilibrium constant:

$$pK^0_{T_{act}} = pK^0_{T_{ref}} + \frac{\Delta H^0_{r,T_{ref}}}{2.3026 \cdot R} \cdot \frac{T_{ref} - T_{act}}{T_{ref} \cdot T_{act}}$$

Influence of pH-changes on equilibrium equation:

$$\Delta G^{0'}_r = \Delta G^0_r - 2.3026 \cdot R \cdot T \cdot q \cdot pH_{act} \qquad (4)$$

Influence of pH-changes on disequilibrium equation:

$$\Delta G_r = \Delta G^0_r + 2.3026 \cdot R \cdot T \cdot \left(\log\ Q'_{neq} - q \cdot pH_{act}\right) \qquad (5)$$

or

$$\Delta G_r = 2.3026 \cdot R \cdot T \cdot \left(pK^0 + \log\ Q'_{neq} - q \cdot pH_{act}\right) \qquad (5)$$

Influence of changes in solute concentrations on solubility products:
(follows from equilibrium equation):

$$pK'_S = pK^{0'}_S - \log\ (\prod_j f_j^{v_j})$$

or

$$pK'_S = pK^{0'}_S + \sum_j \frac{v_j \cdot A \cdot z_j^2 \cdot \sqrt{I}}{1 + a_j \cdot B \cdot \sqrt{I}}$$

Influence of changes in solute concentrations on precipitation-dissolution reactions:
(follows from disequilibrium equation):

$$\Delta G_r = R \cdot T \cdot \ln \frac{IAP}{K'_S}$$

dissolution if $\Delta G_r < 0$ or $\frac{IAP}{K'_S} < 1$

precipitation if $\Delta G_r > 0$ or $\frac{IAP}{K'_S} > 1$

saturation equilibrium if $\Delta G_r = 0$ or $\frac{IAP}{K'_S} = 1$

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Influence of changes in pH, I (ionic strength) and T on the species composition of the carbonate-bicarbonate-carbonic acid equilibrium:

$$\left[CO_3^{2-}\right] = \left[C_T\right] \cdot \frac{K'_{a_1} \cdot K'_{a_2}}{10^{-2pH} + K'_{a_1} \cdot 10^{-pH} + K'_{a_1} \cdot K'_{a_2}}$$

$$\left[HCO_3^-\right] = \left[C_T\right] \cdot \frac{K'_{a_1} \cdot 10^{-pH}}{10^{-2pH} + K'_{a_1} \cdot 10^{-pH} + K'_{a_1} \cdot K'_{a_2}}$$

$$\left[H_2CO_3\right] = \left[C_T\right] \cdot \frac{10^{-2pH}}{10^{-2pH} + K'_{a_1} \cdot 10^{-pH} + K'_{a_1} \cdot K'_{a_2}}$$

Influence of changes in solute concentrations on disequilibrium redox potentials:

$$E = \frac{-\Delta G_r}{n \cdot F}$$

or

$$E = \frac{-\Delta G_r^0}{n \cdot F} - \frac{R \cdot T}{n \cdot F} \cdot \ln Q \qquad \text{and since} \quad \frac{-\Delta G_r^0}{n \cdot F} = E^0, \quad \text{and} \quad \Delta G_r^0 = -R \cdot T \cdot \ln K^0 \qquad (6)$$

$$E = E^0 - \frac{R \cdot T}{n \cdot F} \cdot \ln Q$$

or

$$E = \frac{R \cdot T}{n \cdot F} \cdot \ln \frac{K^0}{Q}$$

Influence of changes in pH on standard redox potentials:

$$E^{0'} = E^0 - \frac{2.3026 \cdot R \cdot T}{F} \cdot \frac{q}{n} \cdot pH \qquad (4)$$

Influence of changes in pH and/or solute concentrations on disequilibrium redox potential:

$$E = -\frac{\Delta G_r^0}{n \cdot F} - \frac{2.3026 \cdot R \cdot T}{n \cdot F} \cdot \left(\log Q'_{red/ox} - q \cdot pH_{act}\right) \qquad (8),(7),(4)$$

or

$$E = E^0 - \frac{2.3026 \cdot R \cdot T}{n \cdot F} \cdot \left(\log Q'_{red/ox} - q \cdot pH_{act}\right)$$

or

$$E = \frac{2.3026 \cdot R \cdot T}{n \cdot F} \cdot \left(pK^0 + \log Q'_{red/ox} - q \cdot pH_{act}\right)$$

Influence of changes in solute concentrations or/and pH on disequilibrium electron activity:

$$pe = \frac{1}{n} \cdot \log K^0 - \frac{q}{n} \cdot pH - \frac{1}{n} \cdot \log Q'_{red/ox} \qquad (7), (4), (9)$$

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Notes and explanations

(1) See list of abbreviations for meaning of terms.

(2) $K^0 \mathrel{\hat{=}} K_{eq} = \dfrac{\prod_j \{P_{jeq}\}^{v_j}}{\prod_i \{S_{ieq}\}^{v_i}}$

(3) $Q = \dfrac{\prod_j \{P_{jneq}\}^{v_j}}{\prod_i \{S_{ineq}\}^{v_i}}$

(4) q is – for H^+-consuming and + for H^+-producing reactions respectively.

(**5**) From $Q = \dfrac{\prod_j \{P'_{jneq}\}^{v_j} \cdot \{H^+\}^q}{\prod_i \{S'_{ineq}\}^{v_i}} = Q'_{neq} \cdot \{H^+\}^q$ follows: $Q'_{neq} = \dfrac{Q}{\{H^+\}^q}$

(6) $Q = \dfrac{\prod_j \{P_{jred}\}^{v_j}}{\prod_i \{S_{iox}\}^{v_i}}$

(7) From $Q = \dfrac{\prod_j \{P'_{jred}\}^{v_j}}{\prod_i \{S'_{iox}\}^{v_i} \cdot \{H^+\}^q \cdot \{e^-\}^n} = Q'_{red/ox} \cdot \{H^+\}^{-q} \cdot \{e^-\}^{-n}$ follows: $Q'_{red/ox} = Q \cdot \{H^+\}^q \cdot \{e^-\}^n$

(8) Electrons which are given off by oxidation half - reactions are assigned a negative sign, electrons which are consumed by reduction half - reactions have a positive sign.

(9) n is always + in the pe - formalism.