P XXX/00 Terms and definitions used with Thermodyn

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

Equilibrium equation: $\Delta G_r = 0$

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

or

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

Disequilibrium equation: $\Delta G_r < 0$

$$\Delta G_r = \Delta G_r^0 + R \cdot T \cdot \ln Q \qquad\qquad\qquad\qquad (3)$$
or
$$\Delta G_r = R \cdot T \cdot \ln \frac{Q}{K^0} \qquad\qquad \frac{Q}{K^0} < 1$$
or
$$Q = K^0 \cdot \exp\left[\frac{\Delta G_r}{R \cdot T}\right]$$
or
$$Q = K^0 \cdot \exp\left[\frac{-E \cdot n \cdot F}{R \cdot T}\right]$$

Influence of temperature changes on equilibrium equation:
$$\Delta G_{r,T_{act}}^0 = \Delta G_{r,T_{ref}}^0 \cdot \frac{T_{act}}{T_{ref}} + \Delta H_{r,T_{ref}}^0 \cdot \frac{T_{ref} - T_{act}}{T_{ref}}$$

Influence of temperature changes on equilibrium constant:
$$pK_{T_{act}}^0 = pK_{T_{ref}}^0 + \frac{\Delta H_{r,T_{ref}}^0}{2.3026 \cdot R} \cdot \frac{T_{ref} - T_{act}}{T_{ref} \cdot T_{act}}$$

Influence of pH-changes on equilibrium equation:

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

Influence of pH-changes on disequilibrium equation:

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

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

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

or

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

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

$$\Delta G_r = R \cdot T \cdot \ln \frac{IAP}{K_S^{'}} \qquad \text{dissolution if} \quad \Delta G_r < 0 \ \ \text{or} \ \ \frac{IAP}{K_S^{'}} < 1$$

$$\text{precipitation if} \quad \Delta G_r > 0 \ \ \text{or} \ \ \frac{IAP}{K_S^{'}} > 1$$

$$\text{saturation equilibrium if} \quad \Delta G_r = 0 \ \ \text{or} \ \ \frac{IAP}{K_S^{'}} = 1$$

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

Influence of changes in pH on standard redox potentials:

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

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:

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

Notes and explanations

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

(2) $K^0 \hat{=} K_{eq} = \dfrac{\underset{j}{\Pi}\left\{P_{jeq}\right\}^{v_j}}{\underset{i}{\Pi}\left\{S_{ieq}\right\}^{v_i}}$

(3) $Q = \dfrac{\underset{j}{\Pi}\left\{P_{jneq}\right\}^{v_j}}{\underset{i}{\Pi}\left\{S_{ineq}\right\}^{v_i}}$

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

(5) From $Q = \dfrac{\underset{j}{\Pi}\left\{P'_{jneq}\right\}^{v_j} \cdot \left\{H^+\right\}^{q}}{\underset{i}{\Pi}\left\{S'_{ineq}\right\}^{v_i}} = Q'_{neq} \cdot \left\{H^+\right\}^{q}$ follows : $Q'_{neq} = \dfrac{Q}{\left\{H^+\right\}^{q}}$

(6) $Q = \dfrac{\underset{j}{\Pi}\left\{P_{jred}\right\}^{v_j}}{\underset{i}{\Pi}\left\{S_{iox}\right\}^{v_i}}$

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

(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.