**extraction (equilibrium) constant**

The extraction constant at zero ionic strength, \( K_{ex}^0 \), is the equilibrium constant of the distribution reaction expressed in terms of the reacting species. Thus, for the gross reaction:

\[
M^{n+}_{aq} + nHL_{org} \rightleftharpoons ML_{n, org} + nH^+_{aq}
\]

in which the reagent HL initially dissolved in an organic phase reacts with a metal ion \( M^n \) in aqueous solution to form a product \( ML_n \) which is more soluble in the organic phase than in water,

\[
K_{ex}^0 = \frac{a_{ML_{n, org}} a^n_{H^+_{aq}}}{a_{M^{n+}_{aq}} a^n_{HL_{org}}}
\]

Notes:
1. When concentrations are used instead of activities or mixed terms are employed as when \( H^+ \) and/or \( M^n \) are measured with an electrode, the appropriate name is extraction constant, symbol \( K_{ex} \), accompanied by a careful definition. \( K_{ex}^0 \) may be termed the thermodynamic extraction constant.
2. The extraction constant is related to other terms relevant to such systems by:

\[
K_{ex} = \frac{D_{ML_n} \beta_n K^n_A}{D_{HL}^n}
\]

where \( \beta_n \) is the overall formation constant of \( ML_n \) and \( K_A \) is the dissociation constant of HL. Where the reagent HL is more soluble in water than the other immiscible phase it may be more convenient to define a special equilibrium constant in terms of \( HL_{aq} \):

\[
K_{ex} = D_{ML_n} \beta_n K^n_A
\]

3. In distribution equilibria involving non-aqueous systems, e.g. liquid \( SO_2 \), molten salts and metals, the mass action equilibrium constant for the relevant extraction process can be identified with \( K_{ex} \) which should be explicitly defined in this context.
4. In actual practice, it may be necessary to include other terms to take into account other complexes formed by auxiliary reagents and the solvation and/or polymerization of the various species. In such cases, \( K_{ex} \) must be defined with reference to the relevant explicit chemical equation. An example is complex
formation between the metal ion and an uncharged crown ether or cryptand molecule followed by ion-pair extraction:

\[ M_{aq}^{n+} + L_{org} + nA_{aq}^- \rightleftharpoons (ML^{n+}A_n^{n-})_{org} \]

\[ K_{ex} = \frac{[ML^{n+}A_n^{n-}]_{org}}{[M^{n+}]_{aq} [L]_{org} [A^-]_{aq}^n} \]

5. Use of Ringbom's 'conditional extraction constant',

\[ K_{ex}^{\text{eff}} = \frac{a_{ii}^{n+} [ML_n']_{org}}{[M']_{aq} [HL']_{org}^n} \]

in conjunction with alpha coefficients is useful.

6. The phases can also be specified by the formula of the solvent or by other symbols (preferably Roman numerals) or by overlining formulae referring to one phase, usually the less polar one. The subscript aq (or w) is often omitted; aq is preferable to w as the latter is appropriate only in English and German.

7. The qualification 'equilibrium' is often omitted.

8. The terms partition constant and distribution constant must not be used in this sense.

Source:
PAC, 1993, 65, 2373 (Nomenclature for liquid-liquid distribution (solvent extraction) (IUPAC Recommendations 1993)) on page 2383
Orange Book, p. 89