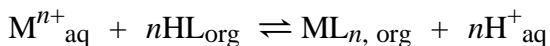


extraction (equilibrium) constant

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



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,

$$K_{\text{ex}}^{\circ} = \frac{a_{ML_{n, \text{org}}} \times a_{H^{+}, \text{aq}}^n}{a_{M^{n+}, \text{aq}} \times a_{HL, \text{org}}^n}$$

Notes:

i. 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}° may be termed the thermodynamic extraction constant.

ii. The extraction constant is related to other terms relevant to such systems by:

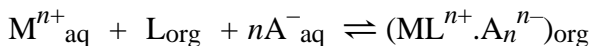
$$K_{\text{ex}} = \frac{D_{ML_n} \beta_n K_a^n}{D_{HL}^n}$$

where β_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} :

$$K_{\text{ex}} = D_{ML_n} \beta_n K_a^n$$

iii. 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.

iv. 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:



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

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

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

in conjunction with alpha coefficients is useful.

vi. 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.

vii. The qualification 'equilibrium' is often omitted.

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

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