

### 9.4.3 Fundamental Parameters

#### **Concentration Factor**

Not recommended. See *Extraction factor*.

#### **Decontamination Factor**

The ratio of the proportion of contaminant to product before treatment to the proportion after treatment. It is the reciprocal of the *enrichment factor*.

#### **Distribution Coefficient**

This term is not recommended as a synonym for *distribution ratio*.

#### **Distribution Constant**

A synonym for *partition ratio*.

#### **Distribution Ratio (in liquid-liquid distribution) (*D*)**

The ratio of the *total* analytical concentration of a solute in the *extract* (regardless of its chemical form) to its total analytical concentration in the other phase.

#### Notes:

- (i) If there is possible confusion with the *extraction factor* or (*mass*) *distribution ratio*, the term *concentration distribution ratio* (symbol  $D_C$ ) should be used, but this is not common usage. This is reasonably compatible with chromatographic nomenclature.
- (ii) The terms *distribution coefficient*, *extraction coefficient* and, where appropriate, *scrubbing coefficient*, *stripping coefficient* are widely used alternatives but are not recommended. If they must be used in a given situation the term *ratio* is preferable to *coefficient*.
- (iii) In equations relating to aqueous/organic systems the organic phase concentration is, by convention, the numerator and the aqueous phase concentration the denominator. In the case of *stripping ratio* the opposite convention is sometimes used but should then be clearly specified.
- (iv) In the past there has been much confusion between the *distribution ratio* as defined above, the value of which varies with experimental conditions, e.g. pH, presence of complexing agents, extent of achievement of equilibrium etc. and the true *partition constant* which is by definition invariable or the partition coefficient or *distribution constant* which apply to a particular chemical species under specified conditions. For this reason the terms *distribution constant*, *partition*

*constant, partition coefficient, partition ratio and extraction constant* should not be used in this context.

- (v) The use of the ratio: *light phase concentration to heavy phase concentration* is ambiguous and is not recommended.
- (vi) The *distribution ratio* is an experimental parameter and its value does not necessarily imply that distribution equilibrium between the phases has been achieved.

### **Enrichment Factor (in liquid-liquid distribution) ( $S$ )**

The factor by which the ratio of the amounts of two substances in the *feed* must be multiplied to give their ratio after treatment.

$$Q_A/Q_B = S_{A,B} (Q'_A/Q'_B)$$

where  $Q_A$  and  $Q'_A$  are the final and initial amounts of species A and  $Q_B$  and  $Q'_B$  are the final and initial amounts of species B. Hence  $S_{A,B} = E_A/E_B$  where  $E$  is the *fraction extracted*. In terms of  $D$ ,  $n$ ,  $r$  (where  $n$  is the number of stages and  $r$  the *phase ratio*).

$$S_{A,B} = \frac{1 - (1 + rD_A)^{-n}}{1 - (1 + rD_B)^{-n}}$$

### **Extractability**

A property which qualitatively indicates the degree to which a substance is extracted.

*Note:* This term is imprecise and generally used in a qualitative sense. It is not a synonym for *fraction extracted*.

### **Extraction Coefficient**

This term is not recommended as a synonym for *distribution ratio*.

### **Extraction (Equilibrium) Constant at Zero Ionic Strength ( $K_{\text{ex}}^0$ )**

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  $\text{ML}_n$  which is more soluble in the organic phase than in water,

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

Notes:

(i) When concentrations are used instead of activities or mixed terms are employed as when  $\text{H}^+$  and/or  $\text{M}^{n+}$  are measured with an electrode, the appropriate name is *extraction constant*, symbol  $K_{\text{ex}}$ , accompanied by a careful definition.  $K_{\text{ex}}^{\circ}$  may be termed the *thermodynamic extraction constant*.

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

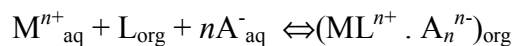
$$K_{\text{ex}} = \frac{D_{\text{ML}_n} \beta_n K_a^n}{D_{\text{HL}}^n}$$

where  $\beta_n$  is the overall formation constant of  $\text{ML}_n$  and  $K_a$  is the dissociation constant of HL. When 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  $\text{HL}_{\text{aq}}$ :

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

(iii) In distribution equilibria involving non-aqueous systems, e.g. liquid  $\text{SO}_2$ , molten salts and metals, the mass action equilibrium constant for the relevant extraction process can be identified with  $K_{\text{ex}}$  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,  $K_{\text{ex}}$  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:



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

(v) Use of Ringbom's "conditional extraction constant",

$$K_{\text{ex}}^{\text{eff}} = \frac{\alpha_{\text{H}^+}^n [\text{ML}'_n]_{\text{org}}}{[\text{M}']_{\text{aq}} [\text{HL}'_n]_{\text{org}}}$$

in conjunction with alpha coefficients is useful. See PAC 66 2501-2512 (1994).

- (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.

### **Extraction Factor ( $D_m$ )**

The ratio of the total mass of a solute in the extract to that in the other phase.

#### Notes:

- (i) It is the product of the (*concentration*) *distribution ratio* and the *appropriate phase ratio*.
- (ii) It is synonymous with the *concentration factor* or *mass distribution ratio*, this latter term being particularly apt.
- (iii) The term *concentration factor* is often employed for the overall *extraction factor* in a process or process step.

### **Fraction Extracted ( $E$ )**

The fraction of the total quantity of a substance extracted (usually by the solvent) under specified conditions, i.e.  $E_A = Q_A/Q'_A$  where  $Q_A$  is the mass of A extracted and  $Q'_A$  is the total mass of A present at the start.

#### Notes:

- (i)  $E$  may be expressed as a percentage, % $E$ .
- (ii) The term *extractability* is qualitative and should not be used as a synonym for *fraction extracted*.
- (iii) If the aqueous phase is extracted with  $n$  successive portions of solvent, the phase volume ratio (solvent/feed) being  $r$  each time, the fraction extracted is given by:

$$E_n = 1 - (rD + 1)^{-n}$$

If  $n = r = 1$ ,  $E_1 = D/(1 + D)$  this expression is a concept of value in chromatography theory.

- (iv) The fraction extracted is also known as the *recovery factor*, especially for a multistage process.

### **Loading Capacity**

The maximum concentration of solute(s) that a *solvent* can contain under specified conditions.

Notes:

- (i) The terms *maximum loading*, *saturation capacity* and *saturation loading* are synonymous.
- (ii) All the above terms should clearly be distinguished from *ultimate capacity*.

### **Mass Distribution Ratio**

See *Extraction factor*.

### **Maximum Loading**

See *Loading capacity*.

### **Partition Coefficient**

This term is not recommended and should not be used as a synonym for *partition constant*, *partition ratio* or *distribution ratio*.

### **Partition Constant ( $K_D^\circ$ )**

The ratio of activity of a given species A in the extract to its activity in the other phase with which it is in equilibrium, thus

$$(K_D^\circ)_A = a_{A,\text{org}} / a_{A,\text{aq}}$$

Its value should not vary with composition but depends on the choice of standard states and on the temperature (and eventually the pressure).

Note: See *Transfer activity coefficient*.

### Partition Ratio ( $K_D$ )

The ratio of the concentration of a substance in a single definite form, A, in the *extract* to its concentration in the same form in the other phase at equilibrium, e.g. for an aqueous/organic system

$$(K_D)_A = [A]_{\text{org}} / [A]_{\text{aq}}$$

#### Notes:

- (i)  $K_D$  is sometimes called the *distribution constant*; this is a good synonym. The terms *distribution coefficient*, *distribution ratio*, *partition constant* and *extraction constant* should not be used as synonyms for *partition ratio*.
- (ii) The use of the inverse ratio (aqueous/organic) may be appropriate in certain cases, e.g. where the organic phase forms the *feed* but its use in such cases should be clearly specified. The ratio of the concentration in the denser phase to the less dense phase is not recommended as it can be ambiguous.
- (iii) If the pure *solvent* and infinitely dilute *feed* are taken as the standard states,  $K_D \rightarrow K_D^\circ$  as the total concentration of dissolved materials decreases.

$\text{pH}_{0.5}$  or  $\text{pH}_{1/2}$

That value of pH in an aqueous phase at which the *distribution ratio* is unity at equilibrium.

*Note:* 50% of the solute is extracted ( $E = 0.5$ ) only when the *phase ratio* is unity.

### Phase Ratio (in liquid-liquid distribution) ( $r$ )

The ratio of the quantity of the *solvent* to that of the other phase.

#### *Notes:*

- (i) Unless otherwise specified the phase ratio refers to the *phase volume ratio*.
- (ii) If other aspects of the phase ratio are employed viz. *phase mass ratio*, *phase flow ratio*, these should be specified.

### Recovery Factor

This term is not recommended. *Fraction extracted* should be used.

### Saturation Capacity

See *Loading capacity*.

### **Saturation Loading**

See *Loading capacity*.

### **Selectivity Coefficient**

This term should not be used as a synonym for *separation factor*.

Note: This term has a specific meaning in relation to ion exchange by solid exchangers. See 9.2.5.5.

### **Selectivity Ratio**

Synonym for *selectivity coefficient*. It should not be used as a synonym for *separation factor*.

### **Separation Coefficient**

This term is not recommended. A synonym for *separation factor*.

### **Separation Factor (in liquid-liquid distribution) ( $\alpha_{A,B}$ )**

The ratio of the respective *distribution ratios* of two extractable solutes measured under the same conditions.

$$\alpha_{A,B} = D_A/D_B$$

#### Notes:

- (i) By convention the solutes designated as A and B in the above are chosen so as to make  $\alpha > 1$ .
- (ii) The term *separation coefficient* is not recommended.
- (iii) The terms *selectivity coefficient* and *selectivity ratio* are not synonymous and should not be used.

### **Stoichiometric Capacity**

See *Ultimate capacity*.

### **Transfer Activity Coefficient ( $\gamma_t$ )**

A term used to quantify the difference in the free energy of a solute ion in two different standard states often in two different liquid phases. The relationship is  $\Delta_t G^0 = \nu R T \ln \gamma_t$

where  $\Delta_t G^\circ$  is the transfer Gibbs energy and  $\nu$  is the number of ions in the solute. See *partition constant*.

Notes:

- (i) See *IUPAC Information Bulletin* No. 34 (1974) for full details.
- (ii) It should not be confused with the *mass transfer coefficient* which represents the specific *rate* of transfer of a species from one phase to another.
- (iii) It does not necessarily imply the physical transfer of a solute between two liquid phases.

**Ultimate Capacity**

The theoretical maximum capacity of a *solvent* containing a given concentration of **extractant** for a solute under any conditions.

Note: Where appropriate the term *stoichiometric capacity* can be used.