The partition of salts (i) between two immiscible solution phases and (ii) between the solid salt phase and its saturated salt solution

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Received: 17 December 2019 / Accepted: 2 March 2020 / Published online: 24 April 2020
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Abstract
The partition of salts between two polar immiscible solvents results from the partition of the cations and anions. Because electroneutrality rules in both phases, the partition of cations is affected by that of anions, and vice versa. Thus, the partition of a salt is determined by the chemical potentials of cations and anions in both phases, and it is limited by the boundary condition of electroneutrality. Whereas the partition of neutral molecules does not produce a Galvani potential difference at the interface, the partition of salts does. Here, the equations to calculate this Galvani potential difference are derived for salts of the general composition $\text{Cat}^{(z_{\text{Cat}})}^{+} \text{An}^{(z_{\text{An}})}^{-}$ and for uni-univalent salts $\text{Cat}^{+} \text{An}^{-}$. The activity of a specific ion in a particular phase can thus be purposefully tuned by the choice of a suitable counterion. Finally, the distribution of a salt between its solid phase and its saturated solution is also presented, together with a discussion of the Galvani potential difference across the interface of the two phases.

Graphical abstract

Keywords  Partition · Partition constant · Ion · Salt · Electrolyte · Galvani potential difference · Ion adsorption · Fajans · Precipitation · Titration

List of symbols

| Latin symbols | Description |
|---------------|-------------|
| $a$           | Activity    |
| $A$           | Neutral compound A |
| $\text{An}^{(z_{\text{An}})^{-}}$ | Anion An with $z$ negative charges |
| $\text{B, C,...}$ | Compounds B, C, etc. |
| $c$           | Molar concentration |
| $c^*$         | Standard concentration (1 mol L$^{-1}$) |
| $\text{Cat}^{(z_{\text{Cat}})^{+}}$ | Cation Cat with $z$ positive charges |
| DCM           | Dichloromethane |

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The partition of salts is of high importance in many fields of science: ion transfer (e.g. of drugs) through membranes, ion transfer catalysis in organic synthesis, and extraction of metal ions in analytical chemistry are just the most common examples.

When the partition of compounds between liquid phases is treated, usually the phrase ‘partition between two immiscible liquid phases’ is used. However, completely immiscible liquids do not exist. That phrase just points to those systems where the mutual miscibility is so small that the phases can be considered as pure phases, at least for a simplified treatment.

### Partition of neutral compounds between two immiscible solution phases

The Nernst distribution law describes the partition of a neutral compound $A$ between two immiscible liquid phases $\alpha$ and $\beta$

$$A_\alpha \rightleftharpoons A_\beta. \quad \text{(Equilibrium I)}$$

An example is the distribution of iodine between water and tetrachloromethane. Walter Nernst published the respective equation in 1891 [1]. In modern terms, it states that the ratio of activities [2] of the compound in the two phases is constant at constant temperature ($T$) and pressure ($p$):

$$K_{p(A),T,p} = a_{A,\beta}/a_{A,\alpha}$$

$K_{p(A),T,p}$ is called the partition constant of $A$, and the upright $p$ in the subscript stands for partition. In
equilibrium, the chemical potentials $\mu_{A,\alpha}$ and $\mu_{A,\beta}$ of the distributed compound A must be the same in both phases:

$$
\mu_{A,\alpha} = \mu_{A,\beta}.
$$

(2)

Remember, the chemical potential is the partial derivative of the Gibbs energy over the amount (unit: mol) of substance (atoms, molecules or ions) (here of A), at constant temperature, pressure and constant amounts (unit: mol) of all other compounds (e.g. B, C, etc.):

$$
\mu_A = \left( \frac{\partial G}{\partial n_A} \right)_{T,P,p_b,n_c\ldots}.
$$

(3)

This means that the chemical potential is a measure of the ability to produce or consume work. Since a system does not produce or consume work when it is in equilibrium, the chemical potentials of A in the phases $\alpha$ and $\beta$ must be equal at equilibrium, as otherwise a flux of A from one phase to the other would occur. Since the chemical potential of A can be split into a standard term $\mu_{\text{ch}}^A$ (the chemical standard potential) and an activity-dependent term:

$$
\mu_A = \mu_{\text{ch}}^A + RT \ln a_A
$$

(4)

it follows from the condition (2) that

$$
\mu_{A,\alpha}^\text{ch} + RT \ln a_{A,\alpha} = \mu_{A,\beta}^\text{ch} + RT \ln a_{A,\beta},
$$

(5)

$$
\mu_{A,\alpha}^\text{ch} - \mu_{A,\beta}^\text{ch} = RT \ln a_{A,\beta} - RT \ln a_{A,\alpha}.
$$

(6)

The difference of chemical standard potentials is a constant:

$$
\mu_{A,\alpha}^\text{ch} - \mu_{A,\beta}^\text{ch} = RT \ln \frac{a_{A,\beta}}{a_{A,\alpha}} = 2.303RT \log \frac{a_{A,\beta}}{a_{A,\alpha}}.
$$

(7)

Since the partition constant has been defined as $K_{p(A),T,P} = \frac{a_{A,\beta}}{a_{A,\alpha}}$ (1), the following equation results from (7) and (1):

$$
K_{p(A),T,P} = \frac{a_{A,\beta}}{a_{A,\alpha}} = \exp \left( \frac{\mu_{A,\beta}^\text{ch} - \mu_{A,\alpha}^\text{ch}}{RT} \right) = \frac{10^{\frac{\Delta_{\alpha\rightarrow\beta}G^\text{ch}_A}{RT}}}{\Delta_{\alpha\rightarrow\beta}G^\text{ch}_A}.
$$

(8)

Equation (8) nicely shows that $K_{p(A),T,P}$ is larger than 1 when $\mu_{A,\alpha}^\text{ch} > \mu_{A,\beta}^\text{ch}$, and smaller than 1 for $\mu_{A,\alpha}^\text{ch} < \mu_{A,\beta}^\text{ch}$. Equation (8) can also be written using the standard Gibbs energy of transfer $\Delta_{\alpha\rightarrow\beta}G^\text{ch}_A$ of A from phase $\alpha$ to phase $\beta$, defined as

$$
\Delta_{\alpha\rightarrow\beta}G^\text{ch}_A = \mu_{A,\beta}^\text{ch} - \mu_{A,\alpha}^\text{ch}.
$$

(9)

Because a Gibbs energy difference always refers to a certain direction of the reaction, the arrow in the subscript indicates here the transfer from phase $\alpha$ to $\beta$. With Eq. (9) it is possible to write Eq. (8) as follows:

$$
K_{p(A),T,P} = \frac{a_{A,\beta}}{a_{A,\alpha}} = 10^{\frac{\Delta_{\alpha\rightarrow\beta}G^\text{ch}_A}{RT}}.
$$

(10)

### Partition of a salt $\text{Cat}^{\text{2+}}_{\text{Cat}} + \text{An}^{\text{2-}}_{\text{An}}$ between two immiscible solution phases

For a very simple reason, the partition of a salt between immiscible solvents is more complex than that of neutral compounds: the two constituents of a salt, i.e. cations and anions, are on one side free in solution, but on the other side, their transfer to the other phase is restricted by the condition of electroneutrality in both bulk phases. The electroneutrality is the boundary condition for the partition. Only in the interfacial region (double layer region), where the two phases meet, is the condition of electroneutrality violated. This causes the occurrence of an interfacial potential difference called Galvani potential difference. A salt $\text{Cat}^{\text{2+}}_{\text{Cat}} + \text{An}^{\text{2-}}_{\text{An}}$ partitions between two polar immiscible solvent phases $\alpha$ and $\beta$ according to

$$
v_{\text{Cat},\alpha}\text{Cat}^{\text{2+}}_{\text{Cat}} + v_{\text{An},\alpha}\text{An}^{\text{2-}}_{\text{An}} \rightleftharpoons v_{\text{Cat},\beta}\text{Cat}^{\text{2+}}_{\beta} + v_{\text{An},\beta}\text{An}^{\text{2-}}_{\beta}.
$$

(Equilibrium II)

Since the stoichiometry of the salt is the same in both phases, i.e. $v_{\text{Cat},\alpha} = v_{\text{Cat},\beta} = v_{\text{Cat}}$ and $v_{\text{An},\alpha} = v_{\text{An},\beta} = v_{\text{An}}$, one can write

$$
K_p \left( \text{Cat}^{\text{2+}}_{\text{Cat}} + \text{An}^{\text{2-}}_{\text{An}} \right)_{T,P} = \frac{a_{\text{Cat}}^{v_{\text{Cat}}}}{a_{\text{Cat}}^{v_{\text{Cat},\alpha}}} \frac{a_{\text{An}}^{v_{\text{An}}}}{a_{\text{An}}^{v_{\text{An},\alpha}}}.
$$

(11)

Equation (11) indicates that the salt is assumed to be completely dissociated in both phases, i.e. no ion pairs exist in the two phases. Ion pairs, e.g. $[\text{Cat}^+\text{An}^-]_{\text{ionpair}}$ of a uni-univalent salt, form when the electrostatic attraction between the opposite charged ions is not overcome by the free energy of solvation of the single ions (see the example of $[\text{TBA}^+\text{pic}^-]$ at the end of this paper). This happens especially in solvents which have a low dielectric constant, i.e. which are rather nonpolar. Neglecting ion pairs is certainly a simplification, as ion pairs are in principle ubiquitous in electrolyte solutions. However, if the liquid phases have a high polarity, their formation may be negligible. When one liquid phase is water (a polar solvent), and the other solvent is also polar, like nitrobenzene, ion pairing can be neglected in both phases. Further, the partition could be affected by complex formation or any other chemical equilibria involving the partitioning ions. All these side reactions are excluded in the present treatment.

Figure 1 shows a scheme of the Equilibrium II as the result of the partition equilibria of the cations and anions.
Although the two bulk phases maintain electroneutrality by having equal numbers of negative and positive charges, at the interface of the two phases a Galvani potential difference builds up if the two partition constants

\[ K_{p}^{(\text{Cat}^{(i)z_{\text{Cat}}} + \text{An}^{(i)z_{\text{An}}})}, T, \rho = \frac{a_{\text{Cat}^{(i)z_{\text{Cat}}} + \beta}}{a_{\text{Cat}^{(i)z_{\text{Cat}}} + \alpha}} \]  

(12)

and

\[ K_{p}^{(\text{An}^{(i)z_{\text{An}}} - \text{Cat}^{(i)z_{\text{Cat}}})}, T, \rho = \frac{a_{\text{An}^{(i)z_{\text{An}}} - \beta}}{a_{\text{An}^{(i)z_{\text{An}}} - \alpha}} \]  

(13)

do not have identical values. When these constants differ from each other, which is the case for almost all salts, a minute charge separation occurs across the interface, resulting in the Galvani potential difference:

\[ \Delta_{a, \beta} \phi = \phi_{\beta} - \phi_{\alpha}, \]  

(14)

where \( \phi_{\alpha} \) and \( \phi_{\beta} \) are the inner electrical potentials of the two phases. The determination of the two equilibrium constants would need to know the activity of each single kind of ion, i.e. of the cations and the anions. The situation at the interface shown in Fig. 1 is to some extent similar to that at the interface of an electrode, where an oxidation and reduction can proceed: quantification of a redox equilibrium at an electrode needs to define the zero point of the Galvani potential difference. For the basics of interfacial electrochemistry and especially electrochemical thermodynamics, we suggest the papers by Läng [3] and Inzelt [4]. In the case of redox equilibria the convention is that the Galvani potential difference at the platinum|solution interface of the standard hydrogen electrode is zero. In the case of ion partition equilibria, the commonly accepted convention (there are also other conventions) is that tetraphenylarsonium (TPA\(^{+}\)) cations and tetraphenylborate (TPB\(^{-}\)) anions have identical partition constants [5], because they are equally bulky ions and both are single charged:

\[ K_{p}(\text{TPA}^{+}), T, \rho = K_{p}(\text{TPB}^{-}), T, \rho. \]  

(15)

Partition of this salt produces a zero cell voltage (see the end of this text) of the electrochemical cell:

\[ M_{1} \| E_{1} \| \text{salt bridge 1} \| \text{phase } \alpha \| \text{phase } \beta \| \text{salt bridge 2} \| E_{2} \| M_{2} \]

\( M_{1} \) is the metal phase of reference electrode 1, \( E_{1} \) is the electrolyte of reference electrode 1, \( M_{2} \) is the metal phase of reference electrode 2, \( E_{2} \) is the electrolyte of reference electrode 2, the vertical bar \( \| \) symbolises a phase boundary, and the dashed vertical bar stands for a junction between miscible solutions. When the two reference electrodes are identical, the measured cell voltage is the Galvani potential difference across the interface of \( \alpha \) with \( \beta \) defined as \( \Delta_{a, \beta} \phi = \phi_{\beta} - \phi_{\alpha} \), plus the diffusion potentials at the junctions of the different solutions. The latter can be minimised, so that the Galvani potential difference between the phases \( \alpha \) and \( \beta \) is the major contribution. The calculation of the partition constant \( K_{p}(\text{Cat}^{(i)z_{\text{Cat}}} + \text{An}^{(i)z_{\text{An}}}) \), \( T, \rho \) of the salt can be attempted by calculation of \( K_{p}(\text{Cat}^{(i)z_{\text{Cat}}}), T, \rho \) and \( K_{p}(\text{An}^{(i)z_{\text{An}}} - \text{Cat}^{(i)z_{\text{Cat}}}), T, \rho \), as the three constants are related as follows:

\[ K_{p}(\text{Cat}^{(i)z_{\text{Cat}}} + \text{An}^{(i)z_{\text{An}}})}, T, \rho = \frac{a_{\text{Cat}^{(i)z_{\text{Cat}}} + \beta}}{a_{\text{Cat}^{(i)z_{\text{Cat}}} + \alpha}} \frac{a_{\text{An}^{(i)z_{\text{An}}} - \beta}}{a_{\text{An}^{(i)z_{\text{An}}} - \alpha}} = \left( K_{p}(\text{Cat}^{(i)z_{\text{Cat}}}), T, \rho \right)^{z_{\text{Cat}}} \left( K_{p}(\text{An}^{(i)z_{\text{An}}} - \text{Cat}^{(i)z_{\text{Cat}}}), T, \rho \right)^{z_{\text{An}}}. \]

(16)

**Ion partition between two immiscible solution phases**

Since ions are charged particles, the transfer from one phase to another phase involves electric work, when the two phases have different inner electrical potentials. This work, expressed as a molar quantity, is the charge of the ion \( z_{i} \) multiplied by the charge of one mole unit charges (the Faraday constant), multiplied by the difference of inner electric potentials \( \phi_{\beta} \) and \( \phi_{\alpha} \) between the two phases, i.e. \( z_{i} F (\phi_{\beta} - \phi_{\alpha}) \). The sum of chemical and electrical work for the transfer of ions from infinity (outside the respective phases) to the inner of the respective phases is the so-called electrochemical potential, here \( \bar{\mu}_{i, \alpha} \) and \( \bar{\mu}_{i, \beta} \):

\[ \bar{\mu}_{i, \alpha} = \mu_{i, \alpha} + \varepsilon F \phi_{\alpha}, \]  

(17)

\[ \bar{\mu}_{i, \beta} = \mu_{i, \beta} + \varepsilon F \phi_{\beta}. \]  

(18)
The equilibrium condition for ions is the equality of electrochemical potentials, i.e. \( \nu_{i,\beta} \phi_{i,\beta} = \nu_{i,\alpha} \phi_{i,\alpha} \), since the electric work cannot be neglected:

\[
v_{i,\beta} \phi_{i,\beta} + v_{i,\gamma} z_i F \phi_{i,\gamma} = v_{i,\beta} \phi_{i,\beta} + v_{i,\beta} z_i F \phi_{i,\beta}. \tag{19}
\]

When the partition is not affected by any chemical reactions, the stoichiometry of the salt remains unaffected in both phases, and for the cations and anions the relation \( v_{i,\alpha} = v_{i,\beta} \), must hold true:

\[
\nu_{i,\alpha} z_i F \phi_{i,\alpha} = \nu_{i,\beta} \phi_{i,\beta} + v_{i,\beta} z_i F \phi_{i,\beta}. \tag{20}
\]

This allows the calculation of the Galvani potential difference caused by partition of the ions, either cations or anions:

\[
z_i F \phi_{i,\beta} - z_i F \phi_{i,\alpha} = \nu_{i,\alpha} - \nu_{i,\beta}
\]

\[
\Delta_{x,\beta} \phi_i = \phi_{\beta} - \phi_{\alpha} = \frac{\nu_{i,\alpha} - \nu_{i,\beta}}{z_i F}.
\]

Since the chemical potential of a species i is \( \mu_i = \mu_i^{\ominus} + RT \ln a_i \) (Eq. 4), one can write Eq. (22) as follows:

\[
\Delta_{x,\beta} \phi_i = \frac{1}{z_i F} \left( \mu_i^{\ominus, \alpha} + RT \ln a_{i,\alpha} - \mu_i^{\ominus, \beta} - RT \ln a_{i,\beta} \right),
\]

\[
\Delta_{x,\beta} \phi_i = \frac{\mu_{i,\alpha} - \mu_{i,\beta}}{z_i F} + \frac{RT}{z_i F} \ln a_{i,\beta} - \ln a_{i,\alpha}.
\]

The term \( \frac{\mu_{i,\alpha} - \mu_{i,\beta}}{z_i F} \) defines the standard potential of ion transfer (cf. Eq. 9):

\[
\Delta_{x,\beta} \phi_i^{\ominus} = \frac{\mu_{i,\alpha} - \mu_{i,\beta}}{z_i F} = -\Delta_{x,\beta} G_i^{\ominus}
\]

since \( \Delta_{x,\beta} G_i^{\ominus} = \mu_{i,\beta}^{\ominus} - \mu_{i,\alpha}^{\ominus} \) which is the standard Gibbs energy of transfer of the ions from phase \( \alpha \) to \( \beta \), Eq. (24) can be written as follows:

\[
\Delta_{x,\beta} \phi_i = \Delta_{x,\beta} \phi_i^{\ominus} + \frac{RT}{z_i F} \ln a_{i,\beta} - \ln a_{i,\alpha} = -\frac{\Delta_{x,\beta} G_i^{\ominus}}{z_i F} + \frac{RT}{z_i F} \ln a_{i,\beta}
\]

\[
= -\frac{\Delta_{x,\beta} G_i^{\ominus}}{z_i F} + \frac{RT}{z_i F} \ln \frac{1}{K_{p(i), T_P}}.
\]

The \( K_{p(i), T_P} \) used here is defined in Eq. (1) as \( \frac{a_{i,\beta}}{a_{i,\alpha}} \), but one needs to remember that this is the chemical equilibrium constant for which equality of the inner electric potentials of the two phases is a prerequisite. Hence,

\[
\ln K_{p(i), T_P} = \ln \frac{a_{i,\beta}}{a_{i,\alpha}} = -\frac{\Delta_{x,\beta} G_i^{\ominus}}{RT},
\]

\[
K_{p(i), T_P} = e^{-\frac{\Delta_{x,\beta} G_i^{\ominus}}{RT}} = 10^{-\frac{\Delta_{x,\beta} G_i^{\ominus}}{RT}}.
\]

(For comparison, see also Eqs. (8–10)). Alternatively, one can give the relations

\[
\ln K_{p(i), T_P} = \frac{z_i F \Delta_{x,\beta} \phi_i^{\ominus}}{RT},
\]

\[
K_{p(i), T_P} = e^{\frac{z_i F \Delta_{x,\beta} \phi_i^{\ominus}}{RT}} = 10^{\frac{z_i F \Delta_{x,\beta} \phi_i^{\ominus}}{RT}}.
\]

Since \( \ln \frac{\Delta_{x,\beta} \phi_i}{RT} = \ln \frac{a_{i,\beta}}{a_{i,\alpha}} = \frac{\Delta_{x,\beta} G_i^{\ominus}}{RT} \), it follows with Eq. (26) that \( \Delta_{x,\beta} \phi_i = 0 \): \( \Delta_{x,\beta} \phi_i = \frac{\Delta_{x,\beta} G_i^{\ominus}}{z_i F} + \frac{RT}{z_i F} \ln a_{i,\beta} - \ln a_{i,\alpha} = 0 \), which was the condition to define the chemical equilibrium constant.

In Table 1 standard Gibbs energies of ion transfer and the corresponding standard Galvani potential differences are given for selected ions.

The hydropilicity of cations increases with increasing \( \Delta_{w-nb} G_i^{\ominus} \) and with decreasing \( \Delta_{x,\beta} \phi_i^{\ominus} \). The hydropilicity of anions also increases with increasing \( \Delta_{w-nb} G_i^{\ominus} \), but with increasing \( \Delta_{x,\beta} \phi_i^{\ominus} \). The latter is a result of the negative charge of the anions. In the case of the transfer of ions from water to nitrobenzene, increasing values of \( \Delta_{w-nb} G_i^{\ominus} \) imply that fewer ions are transferred to nitrobenzene.

### Table 1: Standard Gibbs energies of transfer of ions from water to nitrobenzene \( \Delta_{w-nb} G_i^{\ominus} \), and the standard Galvani potential differences \( \Delta_{x,\beta} \phi_i^{\ominus} \) (corresponding to \( \Delta_{x,\beta} \phi_i^{\ominus} \) in this text, i.e. \( \Delta_{w,ab} \phi_i^{\ominus} = \phi_i^{\ominus, ab} - \phi_i^{\ominus, cd} \)).

| Ion | \( \Delta_{w-nb} G_i^{\ominus} \) (kJ mol\(^{-1}\)) | \( \Delta_{w,ab} \phi_i^{\ominus} \) (mV) | References |
|-----|---------------------------------|---------------------------------|------------|
| K\(^+\) | 22.65 | -235 | [13] |
| Rb\(^+\) | 19.80 | -205 | [13] |
| Ti\(^+\) | 19.30 | -200 | [13] |
| Cs\(^+\) | 17.80 | -184 | [13] |
| TMA\(^+\) | 9.60 | -99 | [13] |
| TEA\(^+\) | -0.50 | 5 | [13] |
| TBA\(^+\) | -8.20 | 85 | [13] |
| TBP\(^-\) | -35.90 | -372 | [11] |
| Picate | -3.00 | -31 | [13] |
| ClO\(_3\)^- | 8.00 | 83 | [11] |
| F\(^-\) | 18.80 | 195 | [11] |
| Cl\(^-\) | 25.40 | 263 | [13] |
| Cl\(^-\) | 31.40 | 325 | [11] |
Partition of $\text{Cat}^{(z_{\text{Cat}})}\text{An}^{(z_{\text{An}})-}$ between two immiscible solution phases

Now we need to consider the interplay of cation and anion partition: The chemical interaction of the ions with the two solvents is always different for the cations and anions (with the exception of very few salts, like the TPA$^+$TPB$^-$ mentioned above). Therefore, the partition of cations is affected by that of anions, and vice versa. The difference of inner electric potentials $\Delta z_{\beta}\phi_i$ is not zero, as in the theoretical case of single ion partition discussed in connection with Eq. (27). The Galvani potential differences caused by the cations $\Delta z_{\beta}\phi_{\text{Cat}^{(z_{\text{Cat}})+}}$ and anions $\Delta z_{\beta}\phi_{\text{An}^{(z_{\text{An}})-}}$ must be equal to the overall Galvani potential difference $\Delta z_{\beta}\phi\left(\text{Cat}^{(z_{\text{Cat}})+}\text{An}^{(z_{\text{An}})-}\right)$, as only one potential difference can exist at one interface.

$$\Delta z_{\beta}\phi_{\text{Cat}^{(z_{\text{Cat}})+}} = \Delta z_{\beta}\phi_{\text{An}^{(z_{\text{An}})-}} = \Delta z_{\beta}\phi\left(\text{Cat}^{(z_{\text{Cat}})+}\text{An}^{(z_{\text{An}})-}\right)$$

(31)

Now, Eq. (26) can be formulated for the cations

$$\Delta z_{\beta}\phi_{\text{Cat}^{(z_{\text{Cat}})+}} = \Delta z_{\beta}\phi\left(\text{Cat}^{(z_{\text{Cat}})+}\text{An}^{(z_{\text{An}})-}\right) = \Delta z_{\beta}\phi_{\text{Cat}^{(z_{\text{Cat}})+}} \frac{RT}{z_{\text{Cat}}F} \ln \frac{a_{\text{Cat}^{(z_{\text{Cat}})+},\beta}}{a_{\text{Cat}^{(z_{\text{Cat}})+},\beta}}.$$

(32)

For the anions Eq. (26) follows

$$\Delta z_{\beta}\phi_{\text{An}^{(z_{\text{An}})-}} = \Delta z_{\beta}\phi\left(\text{Cat}^{(z_{\text{Cat}})+}\text{An}^{(z_{\text{An}})-}\right) = \Delta z_{\beta}\phi_{\text{An}^{(z_{\text{An}})-}} \frac{RT}{z_{\text{An}}F} \ln \frac{a_{\text{An}^{(z_{\text{An}})-},\beta}}{a_{\text{An}^{(z_{\text{An}})-},\beta}}.$$

(33)

or

$$\Delta z_{\beta}\phi_{\text{An}^{(z_{\text{An}})-}} = \Delta z_{\beta}\phi_{\text{Cat}^{(z_{\text{Cat}})+}} \frac{RT}{z_{\text{Cat}}F} \ln \frac{a_{\text{An}^{(z_{\text{An}})-},\beta}}{a_{\text{An}^{(z_{\text{An}})-},\beta}}.$$

(34)

To solve the equations for $\Delta z_{\beta}\phi\left(\text{Cat}^{(z_{\text{Cat}})+}\text{An}^{(z_{\text{An}})-}\right)$, Eq. (32) has to be multiplied by $z_{\text{Cat}}$, and Eq. (34) by $z_{\text{An}}$:

$$z_{\text{Cat}}\Delta z_{\beta}\phi_{\text{Cat}^{(z_{\text{Cat}})+}} = z_{\text{Cat}}\Delta z_{\beta}\phi_{\text{Cat}^{(z_{\text{Cat}})+}} \frac{RT}{F} \ln \frac{a_{\text{Cat}^{(z_{\text{Cat}})+},\beta}}{a_{\text{Cat}^{(z_{\text{Cat}})+},\beta}}.$$

(35)

$$z_{\text{An}}\Delta z_{\beta}\phi_{\text{An}^{(z_{\text{An}})-}} = z_{\text{An}}\Delta z_{\beta}\phi_{\text{An}^{(z_{\text{An}})-}} \frac{RT}{F} \ln \frac{a_{\text{An}^{(z_{\text{An}})-},\beta}}{a_{\text{An}^{(z_{\text{An}})-},\beta}}.$$

(36)

Now, Eqs. (35) and (36) can be summed up:

$$z_{\text{Cat}}\Delta z_{\beta}\phi_{\text{Cat}^{(z_{\text{Cat}})+}} = z_{\text{Cat}}\Delta z_{\beta}\phi_{\text{Cat}^{(z_{\text{Cat}})+}} \frac{RT}{F} \ln \frac{a_{\text{Cat}^{(z_{\text{Cat}})+},\beta}}{a_{\text{Cat}^{(z_{\text{Cat}})+},\beta}} + z_{\text{An}}\Delta z_{\beta}\phi_{\text{An}^{(z_{\text{An}})-}} \frac{RT}{F} \ln \frac{a_{\text{An}^{(z_{\text{An}})-},\beta}}{a_{\text{An}^{(z_{\text{An}})-},\beta}}.$$

(37)

and hence

$$\left(\frac{z_{\text{Cat}}}{z_{\text{An}}} \Delta z_{\beta}\phi_{\text{Cat}^{(z_{\text{Cat}})+}}\right) + \frac{RT}{F} \ln \frac{a_{\text{Cat}^{(z_{\text{Cat}})+},\beta}}{a_{\text{Cat}^{(z_{\text{Cat}})+},\beta}} - \frac{RT}{F} \ln \frac{a_{\text{An}^{(z_{\text{An}})-},\beta}}{a_{\text{An}^{(z_{\text{An}})-},\beta}}.$$

(38)

Although Eq. (39) is reminiscent of the Nernst equation, the argument of the logarithm is not the partition constant $K_p\left(\text{Cat}^{(z_{\text{Cat}})+}\text{An}^{(z_{\text{An}})-}\right) \beta \left(\text{Cat}^{(z_{\text{Cat}})+}\text{An}^{(z_{\text{An}})-}\right)^{-\beta} = \frac{z_{\text{Cat}}\Delta z_{\beta}\phi_{\text{Cat}^{(z_{\text{Cat}})+}}}{z_{\text{An}} \Delta z_{\beta}\phi_{\text{An}^{(z_{\text{An}})-}}}$. Eq. (39) is the ratio of the partition constants: $\frac{K_p\left(\text{Cat}^{(z_{\text{Cat}})+}\text{An}^{(z_{\text{An}})-}\right) \beta}{K_p\left(\text{Cat}^{(z_{\text{Cat}})+}\text{An}^{(z_{\text{An}})-}\right)^{-\beta}}$. (cf. Eq. 16), but the term $\frac{z_{\text{Cat}}\Delta z_{\beta}\phi_{\text{Cat}^{(z_{\text{Cat}})+}}}{z_{\text{An}} \Delta z_{\beta}\phi_{\text{An}^{(z_{\text{An}})-}}}$ in Eq. (39) is the ratio of the partition constants: $\frac{K_p\left(\text{Cat}^{(z_{\text{Cat}})+}\text{An}^{(z_{\text{An}})-}\right)}{K_p\left(\text{Cat}^{(z_{\text{Cat}})+}\text{An}^{(z_{\text{An}})-}\right)^{-\beta}}$.

Taking into account that the activity $a_i$ is defined as $a_i = f_c \frac{1}{c_i}$, where $f_c$ is the activity coefficient of $i$, $c_i$ is the molar concentration of $i$, and $c^*$ is the standard concentration (1 mol L$^{-1}$), Eq. (39) assumes the form

$$\Delta z_{\beta}\phi_{\text{Cat}^{(z_{\text{Cat}})+}} \frac{RT}{F} \ln \frac{c_{\text{Cat}^{(z_{\text{Cat}})+},\beta}}{c_{\text{Cat}^{(z_{\text{Cat}})+},\beta}} + \frac{RT}{F} \ln \frac{c_{\text{An}^{(z_{\text{An}})-},\beta}}{c_{\text{An}^{(z_{\text{An}})-},\beta}}.$$

(40)

From the stoichiometry of the salt $\text{Cat}^{(z_{\text{Cat}})+}\text{An}^{(z_{\text{An}})-}$ it follows that in the bulk of the two phases the conditions $c_{\text{Cat}^{(z_{\text{Cat}})+},\beta} = \frac{z_{\text{Cat}}}{z_{\text{An}}} c_{\text{An}^{(z_{\text{An}})-},\beta}$ and $c_{\text{Cat}^{(z_{\text{Cat}})+},\beta} = \frac{z_{\text{Cat}}}{z_{\text{An}}} c_{\text{An}^{(z_{\text{An}})-},\beta}$ hold true. With these relations follows
\[ \Delta_x \beta \phi \left( \text{Cat}^{(\mathrm{Cat})^+} \right) = \frac{z \text{Cat} \Delta_x \beta \phi^\circ_{\text{Cat}^{(\mathrm{Cat})^+}}}{(z \text{Cat} + |z\text{An}|)} + \frac{|z\text{An}| \Delta_x \beta \phi^\circ_{\text{An}^{(\mathrm{An})^-}}}{(z \text{Cat} + |z\text{An}|)} \]

Equation (40) can be also applied to the solubility of a salt, when this is considered as the result of distributing the cations and anions between the solid salt phase and the saturated solution: see Sect. “Distribution of ions between the solid salt phase and the salt saturated solution”.

To calculate the partition constant of a redox reaction \( \text{v}_1 \text{Red}_1 + \text{v}_2 \text{Ox}_2 \rightleftharpoons \text{v}_1 \text{Ox}_1 + \text{v}_2 \text{Red}_2 \) with the two redox equilibria \( \text{Ox}_1 + n_1 \text{e}^- \rightleftharpoons \text{Red}_1 \) and \( \text{Ox}_2 + n_2 \text{e}^- \rightleftharpoons \text{Red}_2 \), where the relation \( \text{v}_1 \text{R}_1 = \text{v}_2 \text{H}_2 = z \) holds, and the equilibrium constant is

\[ \log K = \frac{E - E_{\text{Red}_2} - E_{\text{Red}_1}}{RT} \]  

These equations are similar because in both cases two interdependent equilibria determine the overall equilibrium.

In the case of a uni-univalent salt \( \text{Cat}^{(\text{Cat})^+} \), it follows for \( \Delta_x \beta \phi \left( \text{Cat}^{(\text{Cat})^+} \right) \)

\[ \Delta_x \beta \phi \left( \text{Cat}^{(\text{Cat})^+} \right) = \frac{\Delta_x \beta \phi^\circ_{\text{Cat}^{(\text{Cat})^+}} + \Delta_x \beta \phi^\circ_{\text{An}^{(\text{An})^-}}}{2} \]

and for \( K_p \left( \text{Cat}^{(\text{Cat})^+} \right), \)

\[ \log K_p \left( \text{Cat}^{(\text{Cat})^+} \right) = \frac{E}{RT} \left( \Delta_x \beta \phi^\circ_{\text{Cat}^{(\text{Cat})^+}} - \Delta_x \beta \phi^\circ_{\text{An}^{(\text{An})^-}} \right) \]
—"respect" the affinity of the anions, and vice versa. This compromise leads (i) to a potential difference at the interface (if the affinities are not equal, as in the case of the example TPA⁻TPB⁻) and (ii) to different concentrations of the salt in both phases (if the affinities are not identical).

The tuning of partition constants of salts by choosing appropriate combinations of cations and anions is illustrated in Fig. 5: picric acid (2,4,6-trinitrophenol) is a relatively strong acid in aqueous solution (pKₐ around 0.4). Although the picrate anion (2,4,6-trinitrophenolate) is rather hydrophobic, the partition of sodium picrate (Na⁺pic⁻/C₀) between water and dichloromethane (DCM) is such that the salt almost completely stays in water.

The partition constant is

\[ K_{p(Cat^+An^-)} = \frac{\alpha_{(Cat^+An^-)};_{water}}{\alpha_{(Cat^+An^-)};_{DCM}} \]

\[ = 2.5 \times 10^{-5} \] [7]. This is illustrated by Fig. 5, where the aqueous phase is strongly yellow, the colour of picrate ions, whereas the DCM phase is colourless. The same result is obtained for the partition of picric acid (see Fig. 5)
Experimental considerations concerning the partition of a salt between two immiscible solution phases

The partition constants of neutral molecules are experimentally accessible without any principal constraints. It is just necessary to have analytical techniques at hand, allowing the determination of the concentration of the partitioned compound in both phases. For salts, this can be done in the same way; however, the individual partition constants of the anions and cations are not so easily accessible. Since the individual partition constants are a measure of the interaction of the individual ions with each of the two solvents, e.g. with water and the organic solvent, it is important to know these data. They provide information about the hydrophilicity/hydrophobicity and oleophilicity/oleophobicity of the ions!

Let us consider a uni-univalent salt, for which

$$K_{p(Cat^+ An^-),T,P} = \frac{a_{Cat^+}a_{An^-}}{a_{Cat^+ An^-}} \approx \frac{c_{Cat^+}}{c_{Cat^+ An^-}}$$

is experimentally accessible by measuring the concentrations $c_{Cat^+}$ and $c_{Cat^+ An^-}$. According to Eq. (44) the relation for a uni-univalent salt is

$$\log K_{p(Cat^+ An^-),T,P} = \ln K_{p(Cat^+),T,P} + \ln K_{p(An^-),T,P}.$$

When $K_{p(Cat^+ An^-),T,P}$ is determined by measuring the salt concentrations in both phases, the partition constant of either the cation must be known to calculate that of the anions, or vice versa. This is a serious problem which can be solved only by making for some salts the extrathermodynamic (i.e. not strictly based on thermodynamics) assumptions that the partition coefficients are identical for the anion and cation. This is reasonable in the case of very bulky organic ions, e.g. tetraphenylarsonium (TBA$^+$) cations and tetraphenylborate (TPB$^-$) anions. The latter salt was first proposed by Grunwald et al. [5]. On the basis of this extrathermodynamic assumption, it is possible to build up a system of consistent $K_{p(Cat^+),T,P}$ and $K_{p(An^-),T,P}$ data from analysis of the salt concentrations in the two phases, when different salt combinations are used, among which are salts with TBA$^+$ cations and TPB$^-$ anions.

The experimental determination of individual ion partition constants can also be achieved with the help of electrochemistry. Dating back to first experiments by Nernst and Riesenfeld [9], now voltammetric techniques [10] are available with which the individual transfer of ions across liquid–liquid interfaces can be measured, and from the characteristic potentials of the voltammograms, the standard potentials of the individual ions can be estimated, of course always relying on an extrathermodynamic assumption, like the mentioned Grunwald assumption [11–14]. These measurements need a four-electrode potentiostat, and they are rather limited with respect to the solvent systems. There exists another electrochemical approach, where an electrochemically generated redox probe drives an ion transfer across a liquid–liquid interface [15–17]. For this, a three-electrode potentiostat is sufficient and the number of solvent systems is considerably larger. A complete discussion of the experimental approaches to measure the individual transfer of ions (i.e. ion partition) cannot be given here, and the interested reader should consult the mentioned sources.

Distribution of ions between the solid salt phase and the salt saturated solution

The solubility of a sparingly soluble salt can be considered as the result of distributing the cations and anion between the solid salt phase (s) and the saturated solution (sol):

$$Cat_s^+ + An_s^- \rightleftharpoons Cat_{sol}^+ + An_{sol}^- \quad (\text{Equilibrium III})$$

Of course, $Cat_s^+$ and $An_s^-$ build up the solid phase $\{Cat^+ An^-\}_s$. Equilibrium III has the following equilibrium constant:

$$K_{p(Cat^+ An^-),T,P} = \frac{a_{Cat^+_{sol}}a_{An^-_{sol}}}{a_{Cat^+_s}a_{An^-_s}}.$$

The exact quantity of the activities of the ions in the solid are not known; however, it is clear that they are constant. The solubility product $K_{sp(Cat^+ An^-),T,P}$ of the salt is

$$K_{sp(Cat^+ An^-),T,P} = a_{Cat^+_{sol}}a_{An^-_{sol}},$$

and this is the relation between the solubility product and the partition constant:
\[ K_{\text{sp}}(\text{Cat}^+\text{An}^-),T,p = K_p(\text{Cat}^+\text{An}^-),T,p \frac{[\text{Cat}^+]^s[\text{An}^-]^s}{[\text{Cat}^+]_s[\text{An}^-]_s} \]  

For the cations, Eq. (26) can be written as follows:

\[ \Delta_{s,\text{sol}} \phi_{\text{Cat}^+} = \Delta_{s,\text{sol}} \phi_{\text{Cat}^+}^{c}\text{Cat}^- + RT \frac{\ln a_{\text{Cat}^+}\text{s}}{F} \]
\[ = \Delta_{s,\text{sol}} \phi_{\text{Cat}^+}^{c}\text{Cat}^- + RT \ln a_{\text{Cat}^+}\text{s} - RT \frac{\ln a_{\text{Cat}^+}\text{sol}}{F} \]

The first and second terms on the right side of the equation can be combined to the formal potential of the cation transfer \( \Delta_{s,\text{sol}} \phi_{\text{Cat}^+}^{c}\text{Cat}^- = \Delta_{s,\text{sol}} \phi_{\text{Cat}^+}^{c}\text{Cat}^- + RT \ln a_{\text{Cat}^+}\text{s} \) (the subscript \( c \) of \( \Delta_{s,\text{sol}} \phi_{\text{Cat}^+}^{c}\text{Cat}^- \) stands for 'conditional' because formal potentials relate to fixed conditions), and thus:

\[ \Delta_{s,\text{sol}} \phi_{\text{Cat}^+} = \Delta_{s,\text{sol}} \phi_{\text{Cat}^+}^{c}\text{Cat}^- + RT \frac{\ln a_{\text{Cat}^+}\text{sol}}{F} \]  

For the anions, Eq. (26) is

\[ \Delta_{s,\text{sol}} \phi_{\text{An}^-} = \Delta_{s,\text{sol}} \phi_{\text{An}^-}^{c}\text{An}^+ - RT \frac{\ln a_{\text{An}^-}\text{s}}{F} \]
\[ = \Delta_{s,\text{sol}} \phi_{\text{An}^-}^{c}\text{An}^+ - RT \ln a_{\text{An}^-}\text{s} + RT \frac{\ln a_{\text{An}^-}\text{sol}}{F} \]

The formal potential of the anion transfer is \( \Delta_{s,\text{sol}} \phi_{\text{An}^-}^{c}\text{An}^+ = \Delta_{s,\text{sol}} \phi_{\text{An}^-}^{c}\text{An}^+ - RT \ln a_{\text{An}^-}\text{s} \). With that follows

\[ \Delta_{s,\text{sol}} \phi_{\text{An}^-} = \Delta_{s,\text{sol}} \phi_{\text{An}^-}^{c}\text{An}^+ + RT \frac{\ln a_{\text{An}^-}\text{sol}}{F} \]  

Like at the liquid|liquid interface, also here only one Galvani potential difference can be established: \( \Delta_{s,\text{sol}} \phi_{\text{Cat}^+} = \Delta_{s,\text{sol}} \phi_{\text{An}^-} = \Delta_{s,\text{sol}} \phi_{\text{Cat}^+\text{An}^-} \). Summing up Eqs. (55) and (57), and substituting activities with the products of activity coefficients and concentrations allows one to calculate \( \Delta_{s,\text{sol}} \phi_{\text{Cat}^+\text{An}^-} \):

\[ \Delta_{s,\text{sol}} \phi_{\text{Cat}^+\text{An}^-} = \frac{\Delta_{s,\text{sol}} \phi_{\text{Cat}^+}^{c}\text{Cat}^- + \Delta_{s,\text{sol}} \phi_{\text{An}^-}^{c}\text{An}^+}{2} + \frac{RT}{2F} \ln \frac{a_{\text{An}^-}\text{sol}}{c_{\text{Cat}^+}\text{sol}} + \frac{RT}{2F} \ln \frac{c_{\text{An}^-}\text{sol}}{c_{\text{Cat}^+}\text{sol}} \]

For the saturated solution of the pure sparingly soluble salt, the concentration of the cations equals the concentration of the anions (no excess of one ion sort) in the solution.

In the equilibrium, \( \Delta_{s,\text{sol}} \phi_{\text{Cat}^+\text{An}^-} \) must be zero, because in both phases an excess of cations or anions does not exist. It can be also shown that \( \Delta_{s,\text{sol}} \phi_{\text{Cat}^+\text{An}^-} \) is zero, when the following relations are considered: Defining the two partition constants \( K_{p,\text{Cat}^+} = \frac{a_{\text{Cat}^+}\text{s}}{a_{\text{Cat}^+}\text{sol}} \) and \( K_{p,\text{An}^-} = \frac{a_{\text{An}^-}\text{s}}{a_{\text{An}^-}\text{sol}} \) and taking into account that the activities in the solid are constant (although not necessarily equal) gives \( a_{\text{Cat}^+}\text{sol} = \sqrt{K_{sp}} = K_{p,\text{Cat}^+} a_{\text{Cat}^+}\text{s} \) and \( a_{\text{An}^-}\text{sol} = \sqrt{K_{sp}} = K_{p,\text{An}^-} a_{\text{An}^-}\text{s} \). Using the relation between equilibrium constants and the formal Galvani potentials yields

\[ RT \ln \left( \frac{K_{p,\text{Cat}^+} a_{\text{Cat}^+}\text{s}}{K_{p,\text{An}^-} a_{\text{An}^-}\text{s}} \right) = F \Delta_{s,\text{sol}} \phi_{\text{Cat}^+\text{An}^-} = \frac{RT}{2F} \ln \frac{a_{\text{An}^-}\text{sol}}{c_{\text{Cat}^+}\text{sol}} + \frac{RT}{2F} \ln \frac{c_{\text{An}^-}\text{sol}}{c_{\text{Cat}^+}\text{sol}} \]

When anion addition is considered, the concentration \( c_{\text{Cat}^+}\text{sol} \) can be substituted by

\[ c_{\text{Cat}^+}\text{sol} = \frac{K_{sp}}{c_{\text{An}^-}\text{sol}} \]

Inserting Eq. (61) in Eq. (60) gives

\[ \Delta_{s,\text{sol}} \phi_{\text{Cat}^+\text{An}^-} = \frac{RT}{2F} \ln \frac{c_{\text{An}^-}\text{sol}}{K_{sp}} + \frac{RT}{2F} \ln \frac{c_{\text{An}^-}\text{sol}}{c_{\text{Cat}^+}\text{sol}} \]

Equation (62) nicely shows that the potential difference at the saltsolution interface \( \Delta_{s,\text{sol}} \phi_{\text{Cat}^+\text{An}^-} = \phi_{\text{sol}}(\text{Cat}^+\text{An}^-) - \phi_{\text{sol}}(\text{Cat}^+\text{An}^-) \) becomes positive. In the case of addition of the cations to the solution (e.g. addition of silver nitrate to the saturated solution of silver chloride), the potential difference is

\[ \Delta_{s,\text{sol}} \phi_{\text{Cat}^+\text{An}^-} = \frac{RT}{2F} \ln \frac{K_{sp}}{c_{\text{Cat}^+}\text{sol}} + \frac{RT}{2F} \ln \frac{c_{\text{An}^-}\text{sol}}{c_{\text{Cat}^+}\text{sol}} \]
i.e. the potential difference becomes negative. Figure 6 illustrates the dependencies (62) and (63) for the case of the silver halides AgCl, AgBr and AgI. Since the interfacial potential difference is defined as

\[ \Delta_{s,\text{sol}} \phi_{\text{Cat}^+\text{An}^-} = \phi_{\text{sol},\text{Cat}^+\text{An}^-} - \phi_{s,\text{Cat}^+\text{An}^-}, \]

a positive sign of \( \Delta_{s,\text{sol}} \phi_{\text{Cat}^+\text{An}^-} \) means a negatively charged surface of the silver halides with respect to solution, and vice versa. In the case of titrations of halides with silver ions, the sign of \( \Delta_{s,\text{sol}} \phi_{\text{Cat}^+\text{An}^-} \) changes at the equivalence point. Before the equivalence point \( \Delta_{s,\text{sol}} \phi_{\text{Cat}^+\text{An}^-} \) has a positive sign, i.e. the solid AgX is negatively charged. After the equivalence point, when silver ions are in excess, \( \Delta_{s,\text{sol}} \phi_{\text{Cat}^+\text{An}^-} \) has a negative sign, i.e. the surface of the silver halides is positively charged. This is used in the Fajans methods [18–20] of indication using adsorption indicators, where, as an example, fluorescein anions are used as they are adsorbed on the positively charged surface of silver halides. The adsorption changes the colour of the silver halide precipitate, which serves as indication of the equivalence point. In Fig. 6 deviations between concentrations and activities are not taken into account.

At this point, it is interesting to note the similarities of the solid salt/solution interface with the processes underlying the function of the glass electrode: whereas in the case of the silver halides, the cations and anions are capable of partitioning, in the case of the glass electrode, only the cations, i.e. the protons, can partition and the anions, i.e. the “surface silicate groups”, are unable to partition because they are immobile. This results in the well-known pH response of the Galvani potential difference at glass-solution interfaces [21–23].

**Conclusions**

In this lecture text the partition of salts between two immiscible solution phases is presented, and the equation describing the Galvani potential difference across the liquid-liquid interface is derived. The meaning of standard potentials of transfer of single ions from one solution phase to the other is discussed on the basis of an extrathermodynamic assumption. Further, some experimental details of the determination of the standard potentials of ions are mentioned. Finally, the equilibrium of a solid salt phase with its saturated solution phase is presented on the basis of ion partition equilibria, and the resulting surface charge of the solid phase is discussed in connection with adsorption indicators.

In this text, the structure of the double layers at the interfaces could not be considered.

**Acknowledgements** Open Access funding provided by Projekt DEAL. We are very thankful for many helpful suggestions provided by PD. Dr. Gudrun Scholz, Nico Heise, Javier Roman Silva, and Karupasamy Dharmaraj.

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