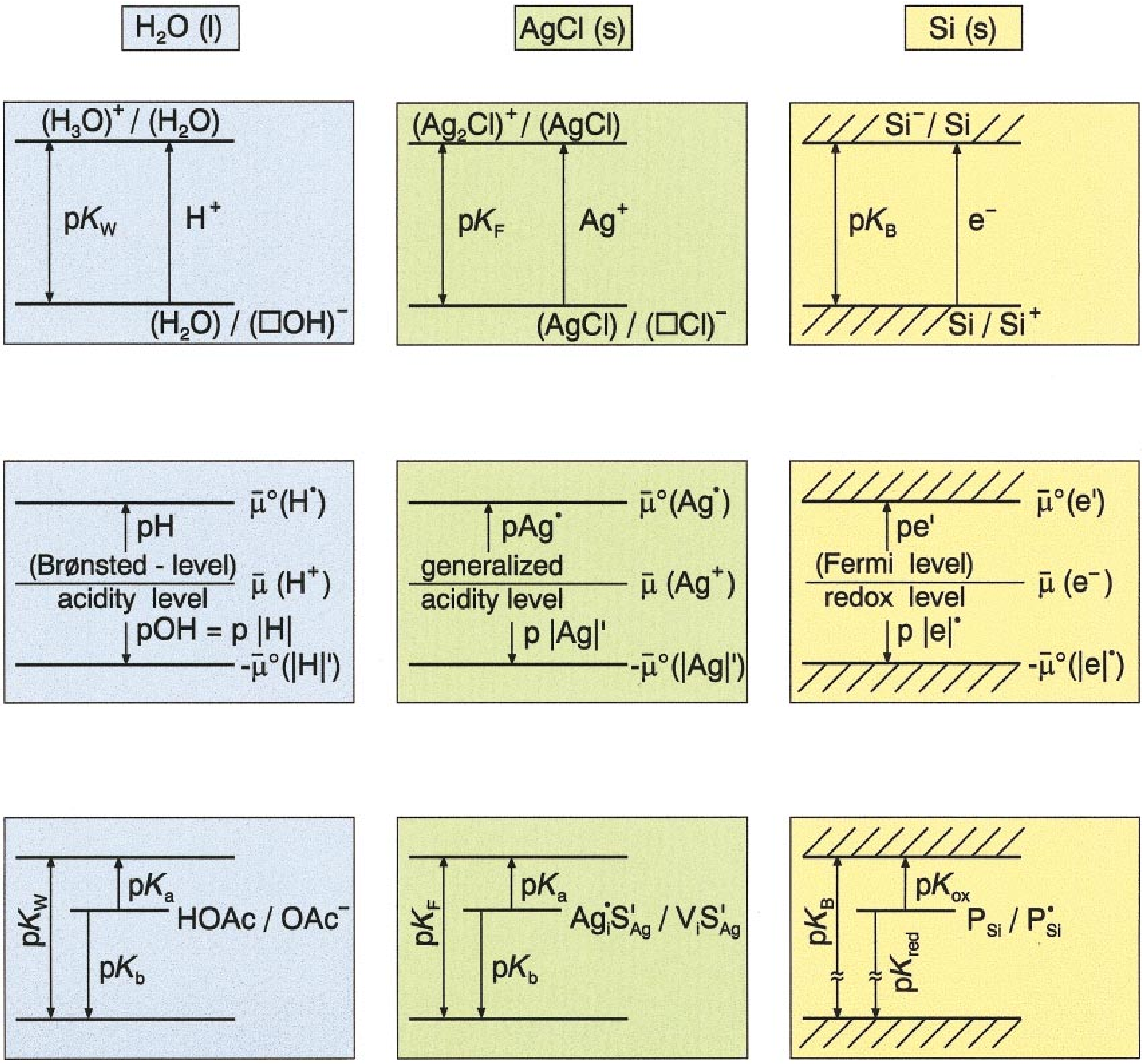

In the same way as the concentration of protonic charge carriers characterizes the acidity (basicity) of water and in the same way as the electronic charge carriers characterize the redox activity, the concentration of elementary ionic charge carriers, that is, of point defects, measure the acidity (basicity) of ionic solids, while associates constitute internal acids and bases.

The definition of acidity/basicity from the (electro-)chemical potential of the exchangeable ion, and, hence, of the defects, leads to a generalized and thermodynamically firm acid–base concept that also allows to link acid–base scales of different solids.

Acid – Base Centers and Acid – Base Scales in Ionic Solids

Joachim Maier*[a]

Abstract: For the case of ionic crystals it is shown to be most straightforward and consistent to define acidity/basicity by the (electro-)chemical potential of the respective ion, in a similar fashion to the way that the Fermi level (i.e., electrochemical potential of the electron) characterizes the redox state. The isomorphy is explicitly expressed by using the energy-level diagrams introduced for electrons in semiconductor physics. Without having to make further assumptions it is possible 1) to compare acidity/basicity between different solids, 2) to link internal and surface acidity/basicity, and 3) to establish acidity/basicity scales for ionic solids. The point defects are revealed to be the natural acidic and basic elementary centers, and associates between them to be the internal acids/bases exchanging these elementary centers. Even though acidity/basicity is an overall property of the solid, the number of point defects (if dilute) directly represents these properties in the same way as H^+ or OH^- accomplish this for aqueous solutions.

Keywords: acidity • basicity • ionic crystals • point defects • solid-state structures • thermodynamics

Introduction

The terms acidity and basicity are useful working tools in chemistry as are the terms redox potentials or redox activity, but they are often puzzling too. This is particularly true if the concepts are applied to solids, since in contrast to aqueous solutions, for instance, no reference is made with respect to specific centers representing these properties as a result of their sheer number. Another reason—which is not entirely independent of this—is to be found in the non-thermodynamic approach that is often taken when introducing such terms. The present paper deals primarily with solids and aims to meet different goals:

1) It is stated that the acidity and basicity of ionic crystals is reflected in the concentrations of the point defects in the same way as the acidity (or basicity) level of water is reflected by the concentrations of H^+ and OH^-. Thus the actual elementary acidic and basic centers are species such as vacancies and interstitial ions.[1] Associates (i.e., complex defects) of the point defects play the role of internal acids and bases exchanging these elementary centers. Notwithstanding the fact that the acidity/basicity is mirrored in the concentrations of the point defects, this acidity/basicity is—as a consequence of thermodynamic equilibrium—a property of the overall material, determined by the (electro-)chemical potentials of the ions and, thus, in spatial equilibrium, also reflecting the surface acidity/basicity.[2] All this is treated on a thermodynamic level free of ad-hoc assumptions.
2) The “energy-level” language used in semiconductor physics for the electrons is, appropriately generalized, introduced as a useful means to illustrate the acidity and basicity functions in solids or liquids, and to determine the quantities pK_a, pK_b, pH, pOH, and their solid state analogues.
3) Since the “energy levels” and, thus, the acidity scales depend on the solvent, that is, on the perfect solid under consideration, a method for comparing and converting these scales is desirable. It is shown that this is possible by measuring the contact effects of different solids, for example, through measurements of ionic boundary conductivity.
4) Finally, the thermodynamic analysis shows that it is most straightforward for ionic crystals to restrict acid – base properties to purely ionic exchange reactions, not necessarily of the protons, that is, to Brønsted-like acid – base effects. Thus, in the terminology of references [3, 4] we refer to ionotropic reactions as counterpart to the redox reactions in which only electronic carriers are exchanged. In those cases in which the reaction with a certain species gives rise to both ion and electron exchange, it proves to be most straightforward to use—for the purely heteropolar systems—terms such as redox acids or redox bases (consider, for example, the interaction of hydrogen with a solid generating both H^+ and e^-) to characterize this double function, rather than to extend and generalize the terms acids and bases to species taking part in the electronic transfer process as most explicitly done by Ussanowitsch.[5] Modifications or extensions which are helpful in non-ionic systems (cf. Lewis concept[6, 7]) need not be taken into account, and would, moreover, unnecessarily obscure the situation.

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Much of the confusion concerning acid–base concepts is due to a lack of precise definition. Here we define thermodynamically the acidity/basicity in terms of the (electro-) chemical potential of the respective cation (e.g., proton) or anion. Explicit use of the O^{2-} activity (and thus of the chemical potential of O^{2-}) for the definition of basicity has been made in reference [8], and very recently by Yamaguchi et al.[9] This latter paper is partly based on a critical examination of the basicity of slags by C. Wagner.[10]

Acidic and Basic Centers in Water Viewed as Point Defects

Let us start with some conceptual remarks. The increase of the Gibbs energy at constant pressure and temperature when adding a species j is called its chemical potential μ_j. If electric fields are involved, the total quantity, usually named electrochemical potential, contains an electrical potential term in addition. This term and also the fact that it is not simply possible to add a charged particle to a system leaving the rest unchanged, leads to nontrivial questions which we can leave aside if we consider the bulk and dilute particles. Then, in addition, interactions between charge carriers and the restricted number of available sites can be neglected leading to a chemical potential μ of the charged species j of the form given in Equation (1):[11]

$$\mu_j \;=\; \mu_j^o + RT\ln(c_j/c^o) \tag{1}$$

in which μ_j^o is the standard potential, c_j is the concentration, and c^o is the standard concentration. This equation simply follows from the fact that in such cases the only concentration dependency stems from configurational effects reflected for the random situation by the term on the right-hand side. Different concentration measures and energetic multiplicities result in constant factors which we can include in μ°. Equation (1) applies to ideal gases, dilute particles in liquid solutions, or dilute point defects in ionic solids. It by no means applies to the regular ions of ionic crystals. Let us first consider aqueous solutions. Since pH and related quantities traditionally refer to the decadic logarithm,[12] it will be rational to define the quantity $\bar{\mu} \equiv \mu/(RT\ln 10)$, for which then Equation (2) applies:

$$\bar{\mu}_j \;=\; \bar{\mu}_j^o + \lg(c_j/c_j^o) \tag{2}$$

in which c^o is the standard concentration in the same dimension as c_j, and in the pH scales normally used in water taken as $1\,\mathrm{mol\,L^{-1}}$. Even though other units or even other measures (number of particles per number of available sites) are more straightforward for solids, we will—for the purpose of comparison—adopt this definition also there. If we identify j with H^+ we can then write Equation (3)

$$\bar{\mu}_{H^+} = \bar{\mu}^o_{H^+} - \mathrm{pH} \tag{3}$$

Note again that for simplicity's sake we restrict to dilute solution.[13] Similarly we can write Equation (4)

$$\bar{\mu}_{OH^-} = \bar{\mu}^o_{OH^-} - \mathrm{pOH} \tag{4}$$

meaning that both pH and pOH scale linearly with the respective ionic chemical potentials. [In nondilute cases Eqs. (3) and (4) are useful as definitions.] Using the equilibrium condition for $H^+ + OH^- \rightleftharpoons H_2O$, as well as identity transformations[14, 15] we get Equation (5) (see also Scheme 1).

$$\bar{\mu}_{H^+} = \bar{\mu}_{H_2O} - \bar{\mu}_{OH^-} \equiv -(\bar{\mu}_{OH^-} - \bar{\mu}_{H_2O}) = -\bar{\mu}_{|H|^-} \approx -(\bar{\mu}_{OH^-} - \bar{\mu}^o_{H_2O}) \tag{5}$$

$$\begin{array}{rcll} H_2O + H_2O & \rightleftharpoons & H_3O^+ + OH^- & |-H_2O \\ H_2O & \rightleftharpoons & H^+ + OH^- & |-H_2O \\ \mathrm{Null} & \rightleftharpoons & H^+ + |H|^- & \end{array}$$

$$\left(|H|^- \text{ is the proton vacancy: } OH^- \text{ minus } H_2O\right)$$

Scheme 1. Successive subtraction of H_2O leads to a minimal formulation of the autoprotolysis reaction in the form of a defect reaction [isomorphic to defect reactions in solids, e.g. Eq. (8) below]. $|H|^-$ is the proton vacancy: OH^- minus H_2O.

Equation (5) reflects the trivial result that pH and pOH add up to the constant pK_w [Eq. (6)].

$$\mathrm{pOH} + \mathrm{pH} \;=\; \mathrm{p}K_w \;=\; \mathrm{p}|H| + \mathrm{pH} \tag{6}$$

(K_w is the autoprotolysis constant of H_2O with $\mathrm{p}K_w \approx \bar{\mu}^o_{H^+} + \bar{\mu}^o_{OH^-} - \bar{\mu}^o_{H_2O}$; the linear combination of the $\bar{\mu}^o$s corresponds to a normalized standard affinity, $\overline{\Delta_w G^o}$.) For the thermodynamic treatment, and in view of the point defects to be considered, it proves much simpler to refer, rather than to OH^-, to the elementary defect "proton vacancy", which we denote by the negative particle $|H|^-$, and which we obtain by subtracting a further water molecule H_2O from OH^- according to $|H|^- \equiv OH^- - H_2O$[16] (see also Scheme 1). The autoprotolysis reaction then takes the simple form given in Equation (7).

$$\mathrm{Null} \rightleftharpoons H^+ + |H|^- \tag{7}$$

Note that $|H|^-$ is not a negatively charged hydrogen but a (negatively charged) negative particle (as the electron hole in semiconductors is a positively charged, negative electronic particle). Please note also that $\bar{\mu}_{|H|^-} = \bar{\mu}_{OH^-} - \bar{\mu}_{H_2O} = -\bar{\mu}_{H^+}$ [Eqs. (5) and (7)] and $\mathrm{pOH} = \mathrm{p}|H|^-$, while $\bar{\mu}^o_{|H|^-} \equiv \bar{\mu}^o_{OH^-} - \bar{\mu}^o_{H_2O} \neq -\bar{\mu}^o_{H^+}$.[17]

Point Defects Viewed as Acidic and Basic Centers in Solids

Let us now turn to solids and first consider the redox centers. The elementary intrinsic electronic carriers in solids are excess electrons (e') or holes, designated as $|e|^\bullet$, or more usually as $h^\bullet$. The Fermi level, $\bar{\mu}_{e^-}$ which we may also call "electronicity" level or redox level can in equilibrium also be written as $(\bar{\mu}_{e^-} =)\bar{\mu}_{e'} = -\bar{\mu}_{h^\cdot}$.[18, 19] (Note that old-fashioned charge notations are used to denote the effective charge which was not necessary for the neutral H_2O as solute.) We recognize the far-reaching isomorphy by replacing H^+ by e'

and OH^-, or more precisely $|H|^-$, by $|e|^\bullet$, that is, $h^\bullet$. The internal fundamental redox reaction is given by Equation (8).

$$\mathrm{Null} \rightleftharpoons e' + h^\bullet \tag{8}$$

Similarly as the electronic processes are visualized by the fundamental "energy levels", which are in fact standard (electro)chemical potentials,[20] we can also construct the analogous protonic levels given by the standard acidity/basicity levels $\bar{\mu}^o_{H^+}$ and $-\bar{\mu}^o_{|H|^-}$. Like the redox level ("electronicity") or Fermi level, we can term $\bar{\mu}_{H^+}$ the acidity level ("protonicity") or the Brønsted level. We recognize that the differences of $\bar{\mu}_{H^+}$ to the "energy levels" give pH and pOH, just as the distances of the Fermi level $\bar{\mu}_{e^-}$ to the band edges (i.e., $\bar{\mu}^o_{e'}$ and $-\bar{\mu}^o_{h^\bullet}$) reflect—on a logarithmic scale—the electronic concentrations [see Eqs. (2) and (5)].

What are the corresponding acidic and basic centers in a solid? If the solid is covalent, such as ice, the picture is completely transformable. In ionic solids, owing to the more strictly defined levels, the situation is even better defined. As in the liquid state, excess and lacking protons, H^+, together with dissolved impurities (solutes) form the defects in the solid and represent the acidic and basic centers.[21]

What happens in an ionic crystal? Even though not a realistic example, let us now take a solid HX and artificially assume it were completely ionic (H^+X^-). Then $\bar{\mu}_{H^+} - \bar{\mu}^o_{H^+}$ would be strongly different from $-\lg c_{H^+}$, since the activity of H^+ is by no means identifiable with the concentration. But also here there would be "chemical excitations" (i.e., point defects), which are only present in a dilute state but in a 1:1 correspondence reflecting the acidity. Again we might measure acidity by counting particles. Some of the protons would be excited into interstitial positions forming $H^\bullet$,[22] and would leave behind vacancies $|H|'$. (Now we need to use dots and dashes to distinguish the particles from regular H^+.[17]) Owing to the equivalence of the chemical potential of H^+ as a constituent and of the defect $H^\bullet$, their concentrations express the acidity of the crystal [Eq. (9)].

$$\bar{\mu}_{H^+} = \bar{\mu}_{H^\bullet} = -\bar{\mu}_{|H|'} \tag{9a}$$

$$\bar{\mu}^o_{H^\bullet} - \bar{\mu}_{H^\bullet} = \mathrm{pH}^\bullet \tag{9b}$$

$$\bar{\mu}^o_{|H|'} - \bar{\mu}_{|H|'} = \mathrm{p}\,|H|' \tag{9c}$$

(It is now advisable to use the charge symbols also in the pX symbol to avoid confusion with $-\lg[H^+]$ or even $-\lg[H]$.)

Let us consider realistic examples of ionic crystals such as AgCl. The internal disorder reaction is the Frenkel reaction, which reads in Schottky nomenclature [Eq. (10)] as

$$\mathrm{Null} \rightleftharpoons \mathrm{Ag}^\bullet + |\mathrm{Ag}|' \tag{10}$$

(describing the internal disorder of regular silver ions into interstitial sites forming interstitial $Ag^\bullet$ and the vacancy defect $|Ag|'$; dash and dot indicate the relative charge, i.e. charges referred to the regular situation.) Frenkel[23] even speaks of a "dissociation" reaction of the crystal. The term "superionic dissociation" is more appropriate.[24]

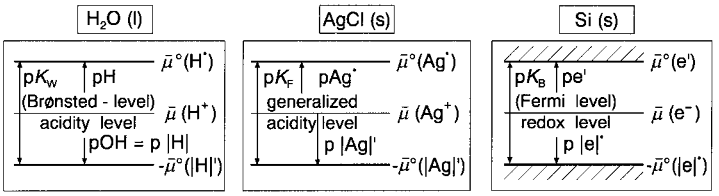
The fact that we have silver ions instead of protons does not change the picture conceptually. Thus we adopt the ionotropic generalization of the Brønsted theory. Evidently Ag^+ interstitials are the acidic particles, while Ag^+ vacancies are the basic particles. Their concentrations will, unlike the overall ion concentration, reflect the acidity/basicity [Eq. (11)].

$$\bar{\mu}_{Ag^+} = \bar{\mu}_{Ag^\bullet} = -\bar{\mu}_{|Ag|'} \tag{11a}$$

$$\bar{\mu}^o_{Ag^\bullet} - \bar{\mu}_{Ag^\bullet} = \mathrm{pAg}^\bullet \tag{11b}$$

$$\bar{\mu}^o_{|Ag|'} - \bar{\mu}_{|Ag|'} = \mathrm{p}\,|\mathrm{Ag}|' \tag{11c}$$

All this is summarized by Figure 1, where we compare the situations with H_2O (l).



$$2H_2O \rightleftharpoons H_3O^+ + OH^- \qquad 2AgCl \rightleftharpoons (Ag_2Cl)^+ + (\square Cl)^- \qquad 2Si \rightleftharpoons Si^+ + Si^-$$

$$2Ag^+Cl^- \rightleftharpoons Ag^0Cl^- + Ag^+Cl^0$$

$$H_2O \rightleftharpoons H^+ + OH^- \qquad Ag_{Ag} + V_i \rightleftharpoons Ag_i^\bullet + V'_{Ag} \qquad 2Si_{Si} \rightleftharpoons Si^\bullet_{Si} + Si'_{Si}$$

(Kröger - Vink notation)

$$\mathrm{Null} \rightleftharpoons H^\bullet + |H|' \qquad \mathrm{Null} \rightleftharpoons Ag^\bullet + |Ag|' \qquad \mathrm{Null} \rightleftharpoons e' + |e|^\bullet$$

(Schottky notation) $(|e|^\bullet \equiv h^\bullet)$

Figure 1. Isomorphy of proton excitation in water, silver ion excitation in AgCl, and electron excitation in Si in the level language, usually used in semiconductor physics (see text). The levels correspond to normalized standard (electro-)chemical potentials [more precisely (electro-)chemical potentials minus configurational contribution]. (Note that the levels are naturally less sharp in a fluid.) The description in terms of a chemical reaction is given in the bottom part. The first-row chemical equations are written in detailed structure element notation. (The number of AgCl units chosen for the Frenkel reaction is arbitrary: A more precise formulation would consider the fact that the vacant sites are of octahedral coordination, while the interstitial sites are the tetrahedral interstices. In the right-hand column the electronic excitation is, in addition to Si, also formulated for AgCl to illustrate that of course both red-ox and acid-base (center column) effects occur in one and the same material.) The center row gives the minimal structure element notation for ionic disorder[38] which is reduced to the relevant atomic centers and, if necessary, uses relative charges. The bottom line uses the building element notation (relative with respect to matter and charge), which is a complete relative notation[20] referring to the difference of real and perfect state (for ionic and electronic disorder).

Internal Acid–Base Equilibria in Solids

Let us push the isomorphy between ions and electrons even further (Figure 2) and consider redox levels in a solid, say a donor D (e.g., P substituting for Si as shown in Figure 2 right). These centers correspond to associates between ionic and electronic particles and can ionize as shown in Equation (12)

$$D \rightleftharpoons D^\bullet + e' \;\Leftrightarrow\; D{-}D^\bullet \rightleftharpoons e' \;\Leftrightarrow\; e^-(D) \rightleftharpoons e' \tag{12}$$

in which e' is the conduction electron and $e^-(D) \equiv D{-}D^\bullet$ the ionizable electron on D. In Equation (12) the chemical potential of the electron at the donor ($\bar{\mu}_{D-D^\bullet} = \bar{\mu}_{e^-(D)}$) equals the Fermi level ($\bar{\mu}_{e'} = \bar{\mu}_{e^-}$) in equilibrium. The distance of the level to the band edge is given by Equation (13)

$$\bar{\mu}^o_{e'} - \bar{\mu}^o_{e^-(D)} = \bar{\mu}^o_{e'} - (\bar{\mu}^o_D - \bar{\mu}^o_{D^\bullet}) = -\lg K_D = \mathrm{p}K_D = \mathrm{p}K_{ox} \tag{13}$$

(Note that $\bar{\mu}^o_{D^\bullet} + \bar{\mu}^o_{e'} - \bar{\mu}^o_D = -\lg K_D \equiv \overline{\Delta_D G^o}$.) In the case of flat donors, that is, small distances, K_D is huge and complete dissociation occurs. Analogous remarks hold for acceptors

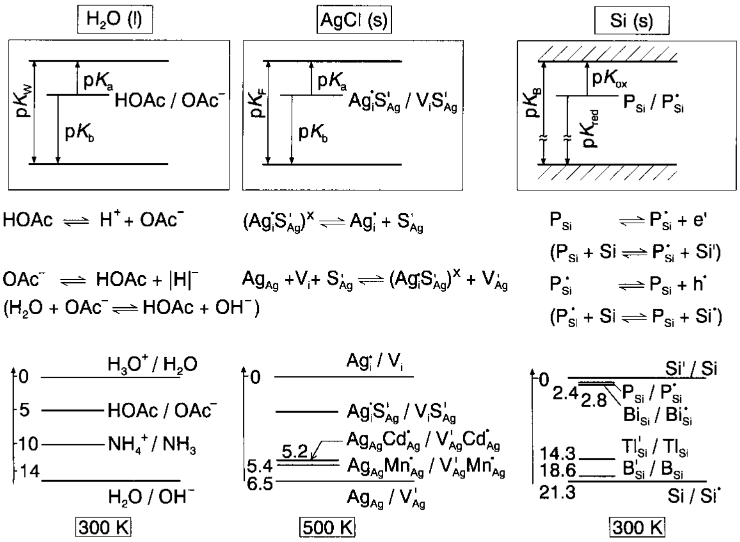


Figure 2. Normalized standard chemical potentials of protons in water, silver ions in crystalline AgCl, and electrons in crystalline Si. The difference between the fundamental levels corresponds to the respective fundamental disorder reaction (autoprotolysis, Frenkel reaction, band–band transfer), while the distance of the levels in the gap to the fundamental levels refers to ion (or electron) transfer from or to acids and bases (or redox states). The first-row reaction formulates the transfer of the ion (proton, $\mathrm{Ag^+}$) or electron from the level under consideration within the gap to the upper fundamental level reflecting $\mathrm{p}K_\mathrm{a}$ or $\mathrm{p}K_\mathrm{ox}$, while the second row refers to the release of the corresponding negative particle ($|\mathrm{H}|^-$, i.e., $\mathrm{OH^-}$; $|\mathrm{Ag}|'$, i.e., $\mathrm{V'_{Ag}}$; or $|\mathrm{e}|^\bullet$, i.e., $\mathrm{h^\bullet}$) and is characterized by the parameters $\mathrm{p}K_\mathrm{b}$ or $\mathrm{p}K_\mathrm{red}$. The units are chosen such that the differences of the levels correspond to decadic logarithms of molar concentrations ($\mathrm{mol\,L^{-1}}$). In the same way the multiplicities of the associates are taken into consideration.[38] Thermodynamic raw data taken from reference [37]. [Naturally, the defect associates are also redox active: The $(\mathrm{Ag_i^\bullet S'_{Ag}})$ complex, for example, also forms a midgap state in the electronic diagram, and an excitation of an electron from a $\mathrm{Cl^-}$ (valence band) to the $\mathrm{Ag^+}$ in the complex demands less energy than the excitation to a regular $\mathrm{Ag^+}$ (conduction band).]

(yielding $\mathrm{p}K_\mathrm{A} \equiv \mathrm{p}K_\mathrm{red}$).[25] Making use of the isomorphy of the relations with regard to the complex acidic and basic centers in water (Figure 2 left), we recognize that similarly the distance of acidic or basic levels to the fundamental $\tilde{\mu}^\mathrm{o}_{\mathrm{H^+}}$ and $\tilde{\mu}^\mathrm{o}_{|\mathrm{H}|^-}$ levels yield the $\mathrm{p}K_\mathrm{a}$ and $\mathrm{p}K_\mathrm{b}$ values, respectively. To give an example: the levels in the left part of Figure 2 correspond to the acid–base pairs $\mathrm{HOAc/OAc^-}$ ($\mathrm{Ac} \equiv \mathrm{CH_3CO}$) and $\mathrm{NH_4^+/NH_3}$ and represent the normalized standard potential of the protons in HOAc or $\mathrm{NH_4^+}$. Flat levels correspond to strong acids, deep levels to weak acids and a mid gap position means pronounced amphoterism.

Now let us turn to acid–base reactions within ionic solids (Figure 2 center).[26] As for the aqueous solutions the internal acids and bases are complex species, associates, which involve the ion under consideration. If we dope AgCl with $\mathrm{Ag_2S}$ we replace Cl by S (yielding a charged substitutional defect) and form additional $\mathrm{Ag^+}$ in the interstitial lattice. At low temperatures the impurity center and the silver interstitial associate to a complex. Since we are now referring to structural details it is better to use structure element notation.[17] The association is then explicitly described by the reaction of $\mathrm{Ag_i^\bullet}$ ($\mathrm{Ag^+}$ on an interstitial site i) with $\mathrm{S'_{Cl}}$ ($\mathrm{S^{2-}}$ on a $\mathrm{Cl^-}$ site) to form the neutral $(\mathrm{Ag_i^\bullet S'_{Cl}})$. At high temperatures this essentially dissociates, that is, the silver ion is released to form a free $\mathrm{Ag_i^\bullet}$ ($\mathrm{Ag^+}$ on an interstitial site), while overcoming the distance to the upper fundamental level. In other words: the complex acts as a silver-ion donor and, thus, as a (generalized) acid. If the distance is small, the acidic strength is high and most of the associates are dissociated even at comparatively low temperatures, the distance being a direct measure of $\mathrm{p}K_\mathrm{ass}$ or $\mathrm{p}K_\mathrm{diss}$, that is, of $\mathrm{p}K_\mathrm{a}$ or $\mathrm{p}K_\mathrm{b}$. In the same way as $\mathrm{NH_4^+}$ is a weaker acid than HOAc, $(\mathrm{Ag_i^\bullet S'_{Cl}})$ is a weaker (generalized) acid than $(\mathrm{Ag_i^\bullet O'_{Cl}})$ (but stronger than $\mathrm{Ag_{Ag}Cd^\bullet_{Ag}}$, see below).

In relative terms the differences to the fundamental levels, that is, the pKs are convenient measures; we do not need to know the absolute positions, as long as we stick to the same solvent. However, if we compare different materials, all quantities differ by the respective values of the standard values. So it is indeed reasonable to term $\tilde{\mu}^\mathrm{o}_{\mathrm{H^+}}$ and $-\tilde{\mu}^\mathrm{o}_{\mathrm{OH^-}}$ the standard acidity levels as well as it is reasonable to term $\mu^\mathrm{o}_{\mathrm{Ag^\bullet}}$ and $-\mu^\mathrm{o}_{|\mathrm{Ag}|'}$ the generalized standard acidity levels or to refer to $\tilde{\mu}^\mathrm{o}_{\mathrm{e'}}$ and $-\tilde{\mu}^\mathrm{o}_{\mathrm{h^\bullet}}$ as the standard electronicity levels. The question of how to relate the different scales in different materials to each other will be taken up below again.

Another important complex in AgCl is the associate of a $\mathrm{Cd^{2+}}$ impurity ($\mathrm{Cd^\bullet_{Ag}}$) with silver vacancies ($\mathrm{V'_{Ag}}$) to form the neutral $(\mathrm{Cd^\bullet_{Ag}V'_{Ag}})$ complex. In our level scheme $(\mathrm{Cd^\bullet_{Ag}V'_{Ag}})$ lies closer to the lower level, which refers to the vacancy ($-\mu^\mathrm{o}_{|\mathrm{Ag}|'}$). The excitation of a regular silver ion to that level or—put differently—the release of the basic species $\mathrm{V'_{Ag}}$ from the complex, corresponds to the dissociation of the complex and is characterized by $\mathrm{p}K_\mathrm{b}$. The parameter $\mathrm{p}K_\mathrm{a} = \mathrm{p}K_\mathrm{F} - \mathrm{p}K_\mathrm{b}$ describes the release of a silver ion next to $\mathrm{Cd^\bullet_{Ag}}$ into an interstitial site to form the vacancy–impurity complex.

Figures 2 (bottom) and 3 give different quantitative examples with respect to acid–base levels in ionic solids. Note that these centers are necessarily complex in the same way as $\mathrm{NH_4^+}$, $\mathrm{HCO_3^-}$, HOAc ($\equiv \mathrm{CH_3COOH}$) and so forth are necessarily complex. Figure 3 shows examples for AgBr as well as the anti-Frenkel disordered fluorides $\mathrm{CaF_2}$ and $\mathrm{SrF_2}$. For these last two the fundamental disorder occurs now in the anion sublattice, in contrast to the silver halides, and the roles of anions and cations, acids and bases are exchanged.

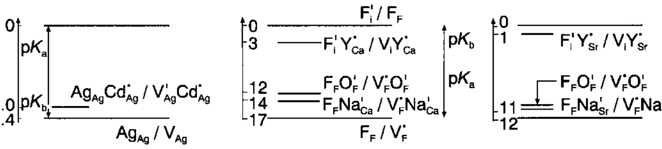


Figure 3. Level pictures for AgBr, $\mathrm{CaF_2}$, and $\mathrm{SrF_2}$. The levels refer to the standard potentials of $\mathrm{Ag^+}$ or $\mathrm{F^-}$ in the respective states. The lower fundamental level refers to the perfect state, while the upper fundamental level refers to the excited state. For the purpose of comparison with $\mathrm{H_2O}$, the units are chosen such that the differences of the levels correspond to decadic logarithms of molar concentrations ($\mathrm{mol\,L^{-1}}$). The multiplicities of the associates are also taken into consideration in AgBr.[38] There the levels closer to the upper level correspond to cation donors and thus to generalized acids and bases, while the lower levels represent efficient acceptors and, hence, bases. For $\mathrm{CaF_2}$ and $\mathrm{SrF_2}$ the roles of cations and anions are exchanged and so are the terms acids and bases.

Complications

Interactions of neutral components with binary solids describe the change of stoichiometry and have an impact on both the ionic and electronic defect budget, for example, the incorporation of a silver excess in AgCl ($Ag + V_i \rightleftharpoons Ag_i^{\bullet} + e'$) or the introduction of oxygen into vacancy-containing oxides ($\frac{1}{2}O_2 + V_O^{\bullet\bullet} \rightleftharpoons O_O + 2h^{\bullet}$).

This interaction involves ionic and electronic processes and, in fact, quantitatively relates the acidity level and the electronicity level ($\mu_{Ag} = \mu_{Ag^+} + \mu_{e^-} = \mu_{Ag^{\bullet}} + \mu_{e'}$). In water such an interaction would, for example, be the solubility of H_2, ($\frac{1}{2}H_2 + H_2O \rightleftharpoons H_3O^+ + e^-$), which is usually not of proper significance.[27] (The analogous reaction of the solvent liquid ammonia can be visualized with the well-known color change.)

In our context it is naturally preferable to term such species redox acids (or redox bases) rather than to generalize the term acids (and bases) to an extent that it is also comprising both ionic and electronic interactions (cf. Ussanowitsch concept). The same holds for internal associates of ionic and electronic defects (such as oxygen vacancies that have trapped one or two electrons).

Let us return to the purely ionic effects and consider a different type of disorder. As regards the Schottky disordered NaCl[28] the situation is similar as discussed for AgCl; however, the fundamental internal dissociation reaction now involves both Na^+ and Cl^- and the level language is not very appropriate. Yet, also here impurity complexes form internal acids and bases the pK_a and pK_b of which are related by the Schottky reaction (pK_s). The association strength of $M_{Na}^{\bullet}$ (i.e., M^{2+} on Na^+ sites) with V'_{Na} decreases, and, thus, the basicity (i.e., the ability of setting free the basic V'_{Na}) increases from Cd^{2+} through Sr^{2+} to Mg^{2+}.

If the solvent is already complex such as Na^+OH^- (complex anion) we face two kinds of fundamental acid–base reactions: one is the dissociation as discussed above ("superionic dissociation"[24]) and the other the ionic dissociation of the covalent OH^- according to $2\,OH_{OH} \rightleftharpoons HOH_{OH}^{\bullet} + O'_{OH}$ leading to the acidic H_2O (in NaOH!) and the basic O^{2-}.

A further illustrative example refers to the water uptake of oxides, typically perovskites, which can make them proton-conducting[9, 29] by the introduction of OH^- groups into the O^{2-} sublattice. Similar as at the surface, this water incorporation leads to the formation of internal OH^- groups. A necessary requirement is (we exclude interstitial OH^- in view of the dense structure) the existence of oxygen vacancies. Let us, in a thermodynamic thought experiment, split the gaseous H_2O into $2\,H^+(g)$, and $O^{2-}(g)$.[29] Then the process consists of filling the oxygen vacancy by O^{2-} to form a regular $O_O^{\times}$, ($O^{2-}(g) + V_O^{\bullet\bullet} \rightleftharpoons O_O^{\times}(g)$), and, second, in bringing the protons into the lattice ($2\,H^+(g) + 2\,O_O^{\times} \rightleftharpoons 2\,OH_O^{\bullet}$), to form OH^- defects (on O^{2-} sites). The first reaction expresses the O^{2-} basicity/acidity of the oxide characterized by the reaction of the acidic $V_O^{\bullet\bullet}$ with the basic O^{2-} (to form O^{2-} effectively neutralized in the crystal lattice), the second expresses the proton acidity/basicity of the lattice (reaction of the $O_O^{\times}$ with the acidic $H^+(g)$ to form the comparatively acidic particle $OH_O^{\bullet}$). Both properties are different, yet coupled through the chemical potential of H_2O.

As already seen when considering NaCl, the level language loses its adequacy in cases in which different ionic species are mobile and exchangeable. In the most general case a variety of internal defect reactions occurs and a variety of (acidic and basic) elementary point defect species have to be taken into account. Since each internal defect reaction corresponds to a specific level picture characterized by an individual fundamental gap, the chemical description in terms of chemical reactions becomes preferable. This is even more serious when multinary compounds are considered, since then we have to speak of different kinds of acidities/basicities. While the validity of the thermodynamic treatment remains untouched, the meaningfulness of the acid/base concept then gets lost. Yet, in most cases indeed one intrinsic defect reaction prevails, while other defects are negligible or frozen-in. Then the acid–base terminology is as useful for the consideration of ion-transfer reactions as redox considerations are to rationalize electron-transfer reactions.

Frequently, acid/base properties of solids are solely understood in terms of surface properties and termed surface acidity or basicity. If we can ignore electric field influences it is now evident that in equilibrium, owing to the spatial constancy of μ_{H^+}, μ_{e^-}, or μ_{Ag^+}, this reflects exactly the same property that is reflected in the interior by point defect concentrations. Moreover, the chemical potential of the surface ions is also reflected by the concentration of the defects, provided they are dilute, within the surface. Owing to the different μ^o's and pK's, their concentrations deviate from that of the bulk.[30] In other words the acid–base scales of bulk and surface are different and can be converted by means of surface thermodynamics which gives the difference $\mu^o(\text{bulk}) - \mu^o(\text{surface})$.[31]

These surface defects should, owing to their high local energy, be catalytically very reactive. In references [32] and [33] indeed the ability of these defects to be effective acid–base catalytic centers has been demonstrated. Since for many reactions both acid/base and redox catalysis should be necessary, it is not surprising that mixed conductors are usually efficient catalysts (which may even be enhanced by the mobilities). Here it is worth mentioning that for very tiny crystals, the chemical potential of the components—and thus also acidity and basicity—is perceptibly influenced by the surface-to-bulk ratio and, hence, will be size dependent . In non-equilibrium cases the (electro-)chemical potential is not the same everywhere. Then basicity/acidity varies locally even on the time average: a relevant example may be high local basicity/acidity of frozen surface defects.

Generally at surfaces, field effects have to be taken seriously, since the surface is charged. References [34] and [35] give a detailed account of how to correlate the concentrations with the proper material and state parameters. The situation is more complicated, but on the other side, it is this charging effect which allows one indeed to determine the difference of the scales (standard levels) between the two solids, namely the difference of the standard acidities (level difference) of the individual species. In these cases we have to identify the Fermi level with the total chemical potential, which also includes field effects, that is, we refer to the electrochemical potential (indicated by a tilde: $\tilde{\mu}$).

Acidity Scales in Different Solids and Acid–Base Reactions of Solids

Let us first consider two solids A and B. If the electronicity level (Fermi level) of A is higher than that of B, electrons will be transferred from A and to B; even though the effect is not large compared to the number of particles in the solid, this is an expression of the fact that A reduces B.

Similarly if A and B are two protonic solids, a higher protonicity (Brønsted level) level in A means that A protonizes B. Thus A is more proton-acidic than B. Again this can be generalized appropriately to anions (O^{2-}) or other cations (Ag^+). The reader may note that this is analogous to the transfer of protons from HOAc to NH_3 in molecular chemistry as shown by Figure 4. The correspondence is perfect if we consider the solid as a giant molecule (the products of OAc^- and NH_4^+ then corresponding to the charged A and B solids).

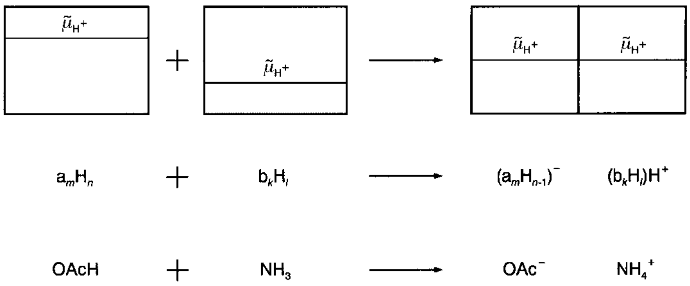


Figure 4. The electrochemical potential ($\tilde{\mu}$) of the respective ion dictates the direction of ion transfer, and, thus, the relative acidity and basicity. If we conceive the solids as giant molecules (solid A: a_mH_n, solid B: b_kH_l) the charge transfer is directly comparable with the protonation of a basic molecule by an acidic molecule.

To compare different solids it is necessary to refer to a common standard state. We chose the gaseous state. Similarly as we can compare the Fermi levels to $\tilde{\mu}_{e^-}$ in the gas phase, we compare the $\tilde{\mu}$'s of a common ion, for example, O^{2-} in oxides with $\tilde{\mu}_{O^{2-}}$ in the gas phase (Figure 5). According to section on acidic and basic centers in water viewed as point defects, the basicity of O^{2-} can be also expressed by the negative electrochemical potential of an oxygen vacancy.

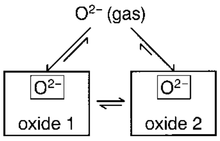


Figure 5. Oxide **1** is more basic than oxide **2**. The electrochemical potential of O^{2-} in **1** is higher than in oxide **2** if isolated, which can be probed by contacting oxide **1** with oxide **2**. The O^{2-} basicity of a variety of oxides can be compared by referring to the O^{2-} in the gas phase. The figure also indicates that the ease to remove an O^{2-} corresponds to the ease of forming an O^{2-} vacancy.

In other words, the higher the O^{2-} basicity is, the easier we can remove an oxygen ion or the more difficult it is to fill a vacancy (or the easier it is to incorporate O^{2-} interstitially). If we dissolve BaO into MgO the ionicity of the oxide ion increases and, leaving other effects aside, the easier the O^{2-} vacancy can be formed. In this sense the ease to remove O^{2-}, that is, the basicity, decreases when the counterpart to the oxygen is made more electronegative. If in a thought experiment M in MO is changed from a very electropositive metal to an electronegative nonmetal, the removal of O^{2-} becomes more and more difficult. The remaining positive charge is progressively more difficult to accommodate (consider, e.g., P_2O_5(s)). (In the elemental solid O_2(s) positively charged oxygen would have to be left!) Besides the pure covalency effect, other influences such as size requirements (cf. pressure) also influence basicity/acidity accordingly.

Note that if both cations and anions are exchangeable we have to specify to what sublattice acidity/basicity refers ($\tilde{\mu}_{M^+}$ or $\tilde{\mu}_{X^-}$). Both properties are connected in each material by μ°_{MX}, which varies if we change the substance.

Let us briefly consider acid–base reactions between solids (see Scheme 2). Even though the thermochemical formalism to fully describe such reactions is straightforward and clear,[14] viewing these equations from the standpoint of the chemical potential of a common ion is very instructive. Let us consider Scheme 2 and follow the O^{2-} basicity: In the first example in Scheme 2, small amounts of BaO are completely dissolved in MgO; the final solid solution has then been made more (O^{2-}) basic relative to MgO by incorporation of the more basic BaO (as already discussed). If we follow the exchange of BaO (Reaction 2) from a more concentrated solid solution to a less concentrated solution, an adjustment of the basicity occurs. The effect is only appreciable, if the amount of the solute is high enough to perceptibly change the mass action constants. Dissolving Na_2O into MgO (Na^+ replacing Mg^{2+}) has an additional electrostatic effect that increases the number of $V_O^{\bullet\bullet}$ (basicity) even for very small amounts (Reaction 3). Reaction 4 shows an acid–base reaction that is restricted to a pure surface-charging reaction. Contacting two comparable compositions of mutually saturated MgO and BaO leads to a contact effect: O^{2-} is transferred from the boundary zone of one phase to the boundary zone of the other phase. (Note that in boundaries acid–base effects are reflected by the combination of both defect concentration changes and electrical potential changes!) In Reaction 5, finally, we form a new compound from the reaction of a basic and an acidic oxide. The picture viewed from O^{2-} basicity concentrates on the partial reaction given in Equation (14)

$\mathrm{MgO} + \varepsilon\mathrm{BaO} \rightleftharpoons \mathrm{MgO(BaO)}_\varepsilon$ Reaction 1

$\alpha\mathrm{MgO(BaO)}_{\mathrm{sss}} + \mathrm{MgO} \rightleftharpoons \mathrm{MgO(BaO)}_\varepsilon$ Reaction 2

$1{-}\varepsilon\mathrm{MgO} + \varepsilon/2\mathrm{Na_2O} \rightleftharpoons \mathrm{Mg}_{1-\varepsilon}\mathrm{Na}_\varepsilon\mathrm{O}_{1-\varepsilon/2}$ Reaction 3

$\mathrm{MgO}_{\mathrm{sss}} + \mathrm{BaO}_{\mathrm{sss}} \rightleftharpoons (\mathrm{MgO})_{\mathrm{sss}} : (\mathrm{BaO})_{\mathrm{sss}}$ Reaction 4

$\mathrm{MgO} + \mathrm{TiO_2} \rightleftharpoons \mathrm{MgTiO_3}$ Reaction 5

Scheme 2. Various types of acid–base reactions as discussed in the text (sss = saturated solid solution).

$$O^{2-}(\mathrm{MgO}) + 2\,O^{2-}(\mathrm{TiO_2}) \rightleftharpoons 3\,O^{2-}(\mathrm{MgTiO_3}) \qquad (14)$$

while a complete quantitative treatment also has to take into account the transfer of Mg^{2+} from MgO into $MgTiO_3$ and of Ti^{4+} from TiO_2 into $MgTiO_3$.

The usefulness of the acid–base consideration is also demonstrated by the following example of a gas–solid boundary effect: In the same way as redox active gases (O_2) can be sensed by their effect on the surface conductivity of semiconducting oxides (SnO_2), ammonia can be sensed by its impact on the surface Ag^+ conductivity of silver halide.[34] As adsorbed oxygen traps electrons, NH_3 traps silver ions to the adsorption layer and increases the vacancy concentration underneath [Eq. (15)].

$$\mathrm{NH_3(base) + Ag_{Ag}(acid) \rightleftharpoons NH_3 \cdots Ag_i^{\bullet}(acid) + V'_{Ag}(base)} \qquad (15)$$

As in the former redox effect (O_2 and SnO_2), this process can be favorably described in the level language. The first effect is essentially a pure redox effect, while the second effect offers the possibility of sensing acid–base active gases.[35]

A final question may be tackled: How can we address the materials parameters through which the different acidity/basicity scales differ?

In reference [36] the contact equilibrium of the two phases MX and MX′ (I, II in Figure 6) is treated, between which an ion can be exchanged. As in the previous example let us here refer to the case that the cation (e.g. Ag^+ in silver halides) is the mobile species. As a consequence of the constancy of the respective electrochemical potential, a partial redistribution of the ion (M^+) has to occur, giving rise to changed acid–base concentrations compensated by an electrical field. This is shown in Figure 6 for the contact of two silver halides. The changed defect concentration, for example, can be measured by the conductance change. If we can suppose that no charge is stored at the core of the interface, the conductance depends (besides mobilities and bulk concentrations) on the differences $\mu^\circ_{\mathrm{I}} - \mu^\circ_{\mathrm{II}}$ in a simple way. It is exactly these differences which distinguish the μ° scales and their standard acidities. For details see reference [36].

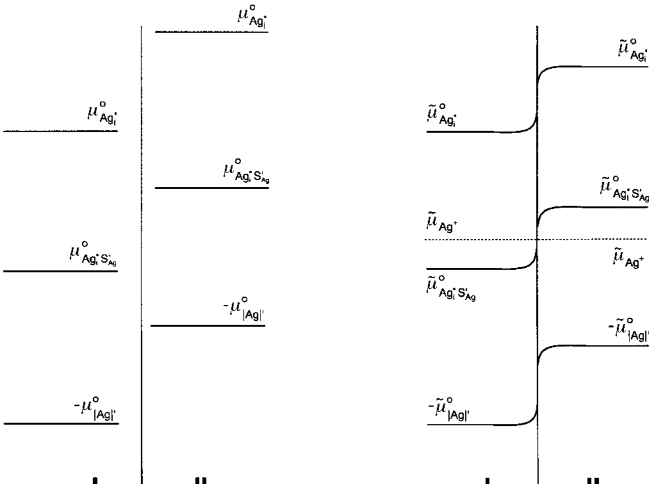


Figure 6. While $\tilde{\mu}_{Ag^+}$, and so the absolute acidity, adjusts at the contact of two phases (two silver halides), there is a jump in the standard state (scale). This jump gives rise to electric fields and concentration changes. The concentration changes can be measured by conductance experiments parallel to the interface.[34] In this way the scales can be compared. Note that while we may define the electrical potential in the bulk of one of the two materials as zero, hence $\mu^\circ = \tilde{\mu}^\circ$, this is not possible then in the other.

Acknowledgement

The author wants to thank Arndt Simon for reading the manuscript and helpful suggestions, and Martin Jansen for discussions.

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[1] Point defect chemistry was founded by a) J. Frenkel, C. Wagner, W. Schottky, *Z. Phys. Chem. B* **1930**, *11*, 163; b) C. Wagner, *Z. Phys. Chem. B* **1936**, *32*, 447; its progress has been summarized in different contributions (see, for example, c) F. A. Kröger, *Chemistry of Imperfect Crystals*, North-Holland, Amsterdam (The Netherlands), **1964**; d) H. Schmalzried, A. Navrotsky, *Festkörperthermodynamik*, VCH, Weinheim (Germany), **1975**; e) J. Maier, *Festkörper—Fehler und Funktion: Prinzipien der Physikalischen Festkörperchemie, Teubner Studienbucher Chemie* (Eds.: C. Elschenbroich, F. Hensel, H. Hopf), Teubner, Stuttgart (Germany), **2000**.

[2] The existence of an electrical equilibrium field complicates the situation in that the chemical potentials of the ions at the surface and in the bulk then differ by the electrical potential difference. Since this can be expressed in terms of the state and materials parameters, surface and bulk acidity/basicity are nonetheless intercorrelated in a defined way.

[3] L. Ebert, N. Konopik, *Oesterr. Chem.-Ztg.* **1949**, *50*, 184; F. Bjerrum, *Angew. Chem.* **1951**, *63*, 527; F. Bjerrum, *Naturwissenschaften* **1951**, *38*, 461.

[4] H. Gehlen, *Z. Phys. Chem.* **1954**, *203*, 125.

[5] M. Ussanowitsch, *Russ. J. Gen. Chem.* **1939**, *9*, 182.

[6] G. N. Lewis, *J. Franklin Inst.* **1938**, *226*, 293.

[7] *Acid–Base Interactions* (Eds.: K. L. Mittal, H. R. Andersen, Jr.), VSP, Utrecht (The Netherlands), **1991**.

[8] M. L. Pearce, *J. Am. Ceram. Soc.* **1964**, *47*, 342; M. L. Pearce, *J. Am. Ceram. Soc.* **1965**, *48*, 175.

[9] S. Yamaguchi, K. Nakamura, T. Higuchi, S. Shin, Y. Iguchi, *Solid State Ionics* **2000**, *136/137*, 191.

[10] C. Wagner, *Metall. Trans. B* **1975**, *6*, 405.

[11] See, for example, R. Haase, in *Physical Chemistry, An Advanced Treatise, Vol. I, Thermodynamics* (Eds.: H. Eyring, D. Henderson, W. Jost), Academic Press, New York (USA), **1971**.

[12] We generally take the definition of $pA^{z+} \equiv -\lg a_{A^{z+}}$ in which the activity $a_{A^{z+}}$ for high dilution of A^{z+} can be replaced by the concentration. For H^+ and OH^- in water, usually the charge number is dropped in the symbol (pH, pOH).

[13] If we deviate from ideal solution, activity coefficients have to be introduced that take account of interionic interactions (according to $c^{1/2}$ (Debye-Hückel) or $c^{1/3}$ (pseudo-Madelung) corrections) or of configurational effects (e.g., Fermi–Dirac corrections).[1e]

[14] From $dG = \Sigma_j \mu_j dn_j = 0$ (G: Gibbs energy, n: mole number) it follows at constant pressure and temperature for a reaction $\mathrm{Null} \rightleftharpoons \Sigma_j \nu_j A_j$ (ν_j: stoichiometric number, negative for reactants, positive for products) together with particle conservation $dn_j/\nu_j = \mathrm{constant}$ that in equilibrium $\Sigma_j \nu_j \mu_j = 0$. Hence for the autoprotolysis reaction $\mu_{H^+} + \mu_{OH^-} = \mu_{H_2O}$. Irrespective of equilibrium conditions we can always write $\mu_{AB} = \mu_{A\,\mathrm{in}\,AB} + \mu_{B\,\mathrm{in}\,AB}$, since AB has been *identically* decomposed into A (in AB) and B (in AB). Unlike the equilibrium condition, this additivity also holds for the standard potentials, thus $\mu_{|H|^-} \equiv \mu_{OH^-} - \mu_{H_2O}$ and $\mu^\circ_{|H|^-} = \mu^\circ_{OH^-} - \mu^\circ_{H_2O}$ (however: $\mu^\circ_{H_2O} \neq \mu^\circ_{H^+} + \mu^\circ_{OH^-}$).

[15] Since the chemical potential of water is only marginally changed by the content of dilute ions: $\mu_{H_2O} \simeq \mu^\circ_{H_2O}$.

[16] J. Maier, *Angew. Chem.* **1993**, *105*, 333; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 313; J. Maier, *Angew. Chem.* **1993**, *105*, 558; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 528.

[17] In defect notation, dots and dashes designate relative charges. Crosses refer to effectively neutral particles and are often left out. In water relative charges and absolute charges are identical, while in ionic solids (M^+X^-) we have to distinguish between absolute charges (M^+) and effective charges. In contrast to ionized but effectively neutral cations on regular positions (sitting in steep potential minima) the comparatively "free" cation, that is, the cation on an "excited" (interstitial) site, is denoted as $M^\bullet$. So this "proper dissociation" on the cation sublattice is described as $\mathrm{Null} \rightleftharpoons M^\bullet + |M|'$. $|M|'$ is the cation

vacancy, which is effectively negatively charged. In addition to this building unit nomenclature in which particles and charges are both defined relative to the perfect structure (Schottky notation), there is a more common structure element nomenclature (Kröger–Vink notation) in which the charges are still relative but the particles are defined as absolute constituents (V: vacancy; the lower index gives the crystallographic site of the perfect structure; i: interstitial site). Thus, in the latter notation, $M^{\bullet}$ is represented by the difference of $M_i^{\bullet}$ and V_i, while $|M|' = V_M' - M_M$.

[18] If we virtually split H_2O into a H^+ part and an OH^- part without decomposing it, that is $H_2O \equiv H^+(H_2O) + OH^-(H_2O)$, then it holds in equilibrium that $\mu_{H^+(H_2O)} = \mu_{H^+}$ where H^+ now refers to the dissociated particle. In the same way in solids the chemical potential of electrons is generally equal to the chemical potential of conduction electrons, that is, $\mu_{e-} = \mu_{e'}$ (and because of reference [14] equal to $-\mu_{h^{\bullet}}$ too). This is simply proven in the following way: first we phenomenologically formulate the implementation of e^- from the gas phase into the solid as $e^-(g) \rightleftharpoons e^-(s)$, and second, we mechanistically formulate this implementation as $e^-(g) \rightleftharpoons e'$. According to reference [14] it follows $\mu_{e^-(s)} = \mu_{e^-(g)} = \mu_{e'}$.

[19] The isomorphism between electrons in solids and protons in solutions was highlighted by A. Rabenau in *Die feste Materie* (Ed.: L. Genzel), Umschau, Frankfurt am Main (Germany), **1973**, p. 223.

[20] W. Schottky in *Halbleiterprobleme IV* (Ed.: W. Schottky), Vieweg, Braunschweig (Germany), **1958**, p. 235.

[21] The real situation in covalent solids is more complex, since in addition to the simple ionic dissociation, there is also site disorder of the neutral species.

[22] With $H_i^{\bullet}$ we mean more accurately excess protons even if the "site" i is very close to the regular one.

[23] J. Frenkel, *Z. Physik* **1926**, *53*, 652.

[24] The term "superionic" takes a rigorous meaning in referring to the dissociation of already "dissociated" particles. It describes the dissociation of the ground state situation ("perfect structure") in which electrically charged particles all sit in their deep potential minima and are immobilized (see also ref. [17]).

[25] The transfer of an electron from the valence band to the acceptor, which thereby becomes ionized, is written as $A \rightleftharpoons A' + h^{\bullet}$. The parameter $pK_A \equiv pK_{red}$ is associated with this reaction. Similarly pK_{ox} addresses the donor ionisation. The sum $pK_{red} + pK_{ox}$ refers to the band–band transfer.

[26] J. Maier, *Solid State Ionics* **2001**, *143*, 17.

[27] The solubility of H_2 or O_2, however, increases significantly if redox active solutes are present. In other words redox active solutes raise the stoichiometric width of impure H_2O considerably. Compare with the analogous tremendous influence of the redox active impurities on the thermodynamic factor of ionic crystals (J. Maier, *J. Am. Ceram. Soc.* **1993**, *76*, 1212).

[28] Schottky disorder means simultaneous formation of cation and anion vacancies as fundamental disorder.

[29] See, for example, K.-D. Kreuer, *Chem. Mater.* **1996**, *8*, 610.

[30] a) R. Defay, I. Prigogine, A. Bellemans, H. Everett, *Surface Tension and Adsorption*, Wiley, New York (USA), **1960**; b) A. I. Rusanov, *Phasengleichgewichte und Grenzflächenerscheinungen*, Akademie-Verlag, Berlin (Germany), **1978**.

[31] See literature on surface thermodynamics, for example, reference [30b].

[32] G. Simkovich, C. Wagner, *J. Catal.* **1962**, *1*, 521.

[33] P. Murugaraj, J. Maier, *Solid State Ionics* **1989**, *32/33*, 993.

[34] J. Maier, *Prog. Solid State Chem.* **1995**, *23*, 171.

[35] J. Maier, *Solid State Ionics* **1993**, *62*, 105.

[36] J. Maier, *Ber. Bunsenges. Phys. Chem.* **1985**, *89*, 355.

[37] J. Corish, P. W. M. Jacobs, *Surf. Defect Prop. Solids* **1973**, *2*, 160; J. Corish, P. W. M. Jacobs, *Surf. Defect Prop. Solids* **1976**, *6*, 219; J. Corish, P. W. M. Jacobs, *J. Phys. Chem. Solids* **1972**, *33*, 1799; S. M. Sze, *Semiconductor Devices*, Wiley, New York (USA), **1985**.

[38] For the purpose of re-scaling the defect concentrations from site fractions (ionic defects) or number density per effective density of states (electronic defects) to the units used here, the molar volume or the effective molar density of states in moles per litre has been used. The multiplicities used are 12 for $(Cd_{Ag}V_{Ag})^{\times}$, 6 for $(Ag_iS_{Cl})^{\times}$ in AgCl and as far as MF_2 (M = Ca, Sr) is concerned: 8 for $(Na_MV_F)^{\times}$, 6 for $(O_FV_F)^{\times}$, and 6 for $(Y_MF_i)^{\times}$; in silicon they are 4 for acceptors and 2 for donors.[37] Also note that the number of possible interstitial sites in AgCl or AgBr is twice the number of regular silver sites, while in CaF_2, SrF_2 it is half that value.

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