Chapter 7
Consequences of Mass Action: Acid–Base Reactions

The concept of mass action can be applied to any transformation of substances. In the case of matter dynamics, it does not matter how we imagine the process in question working at the molecular level: Whether it is by formation or cleavage of chemical bonds, rearranging crystal lattices, migration of particles, transfer of electrons or whole groups of atoms from one type of particle onto the other, etc. In this chapter we will concentrate upon one important example for chemical transformations, namely acid–base reactions, in order to demonstrate that the chemical potential is well suited to describing very specialized and differentiated fields. Acid–base reactions are central to chemistry and its applications; for their quantitative description we introduce the “proton potential” μ_p as a measure of the strength of an acid–base pair. The level equation and the protonation equation are used to describe the behavior of weak acid–base pairs. Subsequently, one important application for acid–base equilibria, the analytic method called acid–base titration, is presented. Finally, the mode of reaction of buffers and indicators is discussed. Buffers play also a significant role in living organisms because even small shifts in the proton potential can there result in disease and death.

7.1 Introduction

The approach used up to now can be applied in the same way for any transformation of substances. In the case of matter dynamics, it does not matter how we imagine the process in question working at the molecular level: Whether it is by formation or cleavage of chemical bonds, rearranging crystal lattices, migration of particles, transfer of electrons or whole groups of atoms from one type of particle onto the other, etc. We will concentrate upon one important example here, namely acid–base reactions, in order to demonstrate that the chemical potential is well suited to describing very specialized and differentiated fields.

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Before introducing the topic in more detail we have to discuss shortly the problems concerning the denomination of hydrogen ions. Hydrogen has three naturally occurring isotopes, called *protium* ^1H, *deuterium* ^2H, and *tritium* ^3H. The corresponding cations are called *proton* (denoted $^1H^+$ or shortly p), *deuteron* ($^2H^+$ or d), and *triton* ($^3H^+$ or t). *Hydron* is the name (recommended by IUPAC in 1988) for positive hydrogen ions H^+ without regard to nuclear mass, especially for the mixture of isotopes formed by natural hydrogen. Traditionally in acid–base chemistry, the term "proton" is used instead of "hydron." But the differences are minute and may be neglected, because more than 99.98 % of the naturally occurring hydrons H^+ are protons p anyway. In this chapter we follow the traditional practice.

7.2 The Acid–Base Concept According to Brønsted and Lowry

According to Johannes Nicolaus Brønsted and Thomas Lowry, an *acid* is a substance or more generally a type of particle (be it neutral or ionic) that tends to release protons p (H^+ ions). It represents a *proton donor* for which we will use the abbreviations HA or BH^+,

$$\mathrm{HA} \rightarrow \mathrm{A}^- + \mathrm{H}^+, \quad \text{and} \quad \mathrm{BH}^+ \rightarrow \mathrm{BH} + \mathrm{H}^+, \quad \text{respectively.}$$

The residual left over from separation is called the *corresponding* or *conjugated base*. The base abbreviated with A^- or BH acts as *proton acceptor*. For general purposes, it is more convenient to use symbols without charge numbers. We will use the abbreviation Ad for the acid (from the Latin acidum) and Bs for the base [(from the Greek βάσιϛ (basis)]:

$$\mathrm{Ad} \rightarrow \mathrm{Bs} + \nu_\mathrm{p}\,\mathrm{p}.$$

Ad and Bs form an *acid–base pair* abbreviated by Ad/Bs. ν_p describes the *proticity*. If $\nu_\mathrm{p} = 1$, one speaks of a monoprotic acid–base pair. However, if $\nu_\mathrm{p} > 1$, it is called polyprotic. Simple examples for monoprotic pairs are HCl/Cl^- and H_3O^+/H_2O:

$$\mathrm{HCl} \rightarrow \mathrm{Cl}^- + \mathrm{H}^+, \quad \mathrm{H_3O}^+ \rightarrow \mathrm{H_2O} + \mathrm{H}^+.$$

In the first case the neutral acid hydrogen chloride HCl tends to release a proton by forming the anionic base Cl^-; in the second the cationic acid H_3O^+ does the same under formation of the neutral base H_2O.

More than one substance can appear in place of the simple one Ad and/or Bs. If we allow the abbreviations Ad and Bs to signify a combination of substances, then the generalized process reads as follows:

$$\overbrace{\mathrm{Ad}' + \mathrm{Ad}'' + \mathrm{Ad}''' + \ldots}^{\mathrm{Ad}} \rightarrow \overbrace{\mathrm{Bs}' + \mathrm{Bs}'' + \mathrm{Bs}''' + \ldots}^{\mathrm{Bs}} + \nu_{\mathrm{p}}\,\mathrm{p}.$$

In the following example, a combined acid appears:

$$\mathrm{CO_2 + H_2O \rightarrow HCO_3^- + H^+}.$$

An acid-base pair Ad/Bs can be considered as a kind of chemical reservoir for protons that is

- Totally full (completely protonated) in the Ad state,
- Totally empty (completely deprotonated) in the Bs state.

Because even the smallest release of protons allows a base to be formed, we can assume from the start that both base and acid are always present to a greater or lesser degree. The separated protons usually do not appear as such. In a following reaction, they are bonded immediately to other particles that function as bases (such as H_2O). In an aqueous solution, the protons appear in the form of oxonium ions H_3O^+. In the case of the dissociation of an acid HA (such as HCl) in water according to $HA \rightarrow A^- + H^+$ protons are directly transferred from the HA molecules to the H_2O molecules (example of a so-called *acid–base reaction*). The following equilibrium is established immediately (within 10^{-8} s):

$$\mathrm{HA|w + H_2O|l \rightleftarrows A^-|w + H_3O^+|w}.$$

Correspondingly, in a reaction of a base B (such as NH_3) with water, protons are transferred from the H_2O molecules to the B molecules:

$$\mathrm{B|w + H_2O|l \rightleftarrows BH^+|w + OH^-|w}.$$

In this case, the water functions as the acid.

We have already seen an impressive example for such an acid–base reaction, namely the ammonia fountain (Experiment 4.12). The formation of an alkaline (basic) milieu in the flask according to

$$\mathrm{NH_3|w + H_2O|l \rightleftarrows NH_4^+|w + OH^-|w}$$

is demonstrated by the change of color of the added indicator (phenolphthalein) from colorless to red violet. We will take a closer look at indicators and their mode of functioning in Sect. 7.7.

7.3 Proton Potential

Basic Idea Obviously, the protons in acid–base reactions are simply transferred from one base B to another B*:

$$BH^+ + B^* \rightleftarrows B + B^*H^+.$$

This is also referred to as a *proton transfer reaction*. The older but ambiguous name *protolytic reaction* is not recommended. According to the general conversion formula, the reaction between gaseous hydrochloric acid and ammonia vapor produces a “sal-ammoniac fog,” a mist of finely distributed ammonium chloride crystals, $NH_4Cl|s$ (Experiment 7.1):

$$HCl|g + NH_3|g \rightarrow \left[NH_4^+\right]\left[Cl^-\right]|s.$$

This means that the definitions given here also hold when no solvent is present.

Most acid–base reactions, however, take place in aqueous solutions. In this case, the second acid–base pair is provided by the solvent water itself (H_3O^+/H_2O or H_2O/OH^-). Despite this, it is possible to assign a chemical potential to the bonded yet exchangeable protons. This is the value established in the equilibrium of the reaction Ad $\rightleftarrows$ Bs + ν_p p, where p denotes protons from any external source. In this particular case we have

$$\mu_{Ad} = \mu_{Bs} + \nu_p \mu_p$$

or

Experiment 7.1 *Formation of “sal-ammoniac fog” from vapors of hydrochloric acid and ammonia*: Concentrated hydrochloric acid is poured in one of the gas-washing bottles; concentrated ammonia solution is poured in the other. By pressing the rubber ball both gases (HCl and NH_3) are unified and the resulting “sal-ammoniac” fog emerges from the small tube.

$$\mu_p = \underbrace{\frac{1}{\nu_p}[\mu_{Ad} - \mu_{Bs}]}_{\mu_p(\text{inside})}, \tag{7.1}$$

respectively. Protons move from outside into the “reservoir” Ad/Bs if $\mu_p > \mu_p$(inside) and in the opposite direction if $\mu_p < \mu_p$(inside). The value of μ_p(inside) is uniquely defined by the chemical potentials μ_{Ad} and μ_{Bs}, meaning it is a characteristic quantity of the acid–base pair under consideration. We express this by adding the name of the pair as argument or subscript:

$$\mu_p(\text{inside}) := \mu_p(\text{Ad/Bs}) := \mu_{p,\text{Ad/Bs}}.$$

The *proton potential* μ_p(Ad/Bs) indicates the strength with which the acid–base pair Ad/Bs tends to transfer protons to any other reservoir. Hence, it is a measure for what is conventionally called the “strength of acid Ad,” or more accurately the *acidic strength* of the pair Ad/Bs. (The tendency to release protons is determined equally by the chemical potential of the acid and that of the corresponding base.) For comparison of acidic strengths of various Ad/Bs pairs, the conditions must be specified. Table 7.1 shows some numerical values $\mu_p^\ominus(\text{Ad/Bs})\left[= \nu_p^{-1}\left(\mu_{Ad}^\ominus - \mu_{Bs}^\ominus\right)\right]$ for *standard conditions* that means 298 K, 100 kPa, and a concentration of

Table 7.1 Standard values of proton potentials of some acid–base pairs (298 K, 100 kPa, 1 kmol m^{-3} in an aqueous solution).

$\text{Ad} \rightleftarrows \text{Bs} + \nu_p\,\text{p}$	$\mu_p^\ominus$(kG)
$HClO_4\|w \rightleftarrows ClO_4^-\|w + H^+$	+57
$HCl\|w \rightleftarrows Cl^-\|w + H^+$	+34
$H_2SO_4\|w \rightleftarrows HSO_4^-\|w + H^+$	+17
$HNO_3\|w \rightleftarrows NO_3^-\|w + H^+$	+8
$H_3O^+\|w \rightleftarrows H_2O\|l + H^+$	0
$HSO_4^-\|w \rightleftarrows SO_4^{2-}\|w + H^+$	−11
$H_2CO_3\|w \rightleftarrows HCO_3^-\|w + H^+$	−21
$C_2H_4OHCOOH\|w \rightleftarrows C_2H_4OHCOO^-\|w + H^+$	−22[a]
$CH_3COOH\|w \rightleftarrows CH_3COO^-\|w + H^+$	−27[b]
$CO_2\|w + H_2O\|l \rightleftarrows HCO_3^-\|w + H^+$	−36
$NH_4^+\|w \rightleftarrows NH_3\|w + H^+$	−53
$HCO_3^-\|w \rightleftarrows CO_3^{2-}\|w + H^+$	−59
$\left[Ca(H_2O)_6\right]^{2+}\|w \rightleftarrows Ca(OH)_2\|s + 4H_2O\|l + 2H^+$	−65
$H_2O\|l \rightleftarrows OH^-\|w + H^+$	−80
$NH_3\|w \rightleftarrows NH_2^-\|w + H^+$	−130
$OH^-\|w \rightleftarrows O^{2-}\|w + H^+$	−165
$H\|g \rightleftarrows e^-\|g + H^+$	−231
$HCl\|g \rightleftarrows Cl^-\|g + H^+$	−289
$HF\|g \rightleftarrows F^-\|g + H^+$	−441

[a] Lactic acid/lactate

[b] Acetic acid/acetate

1 kmol m^{-3} in aqueous solution for both acid and base. For determining such values, for example, the value $\mu_{\text{p}}^{\ominus}(\text{HAc}/\text{Ac}^-)$ of the pair acetic acid/acetate (the abbreviation Ac is used for the acetate group CH_3COO), one first selects the chemical potentials of the acid and the corresponding base at standard conditions from the Table in Sect. A.2.1 in the Appendix or a comparable one. Subsequently, the difference is calculated ($v_{\text{p}} = 1$):

$$\begin{aligned}\mu_{\text{p}}^{\ominus}(\text{HAc}/\text{Ac}^-) &= \tfrac{1}{1}[\mu^{\ominus}(\text{HAc}) - \mu^{\ominus}(\text{Ac}^-)] = (-396.5\ \text{kG}) - (-369.3\ \text{kG}) \\ &= -27.2\ \text{kG}.\end{aligned}$$

Even if the (fictitious) values of acid and base in aqueous solution at a concentration of 1 mol m^{-3} (cp. Sect. 6.2) are used, the proton exchange with the solvent water should be completely inhibited. That means that the acetic acid HAc in the solution in question should only exist as molecule (and not in the ionized form); the acetate ion Ac^-, however, should only exist as ion.

An exception concerning the standard conditions are the pairs H_3O^+/H_2O and H_2O/OH^- where the water that functions as the acid or base (as the case may be) also represents the solvent and is therefore treated as a pure liquid (cf. Sect. 6.3).

We expect that any substance that has protons "impressed" upon it can again release them. Therefore, it follows that in its protonated form, it should be called an acid, and in its original form, its corresponding base. In this regard, protonated water H_3O^+ with its base H_2O is shown in the table as well as the acid H_2O with its base OH^-. This also holds for the hydrogensulfate anion HSO_4^- (protonated H_2SO_4, deprotonated SO_4^{2-}) and for ammonia molecules NH_3 (protonated NH_4^+, deprotonated NH_2^-). Substances that function not only as acids but also as bases are called *amphoteric*.

Acid–base pairs with positive standard value $\mu_{\text{p}}^{\ominus}$ (or more generally positive basic value $\overset{\circ}{\mu}_{\text{p}}$) are considered *strongly acidic* and ones with $\mu_{\text{p}}^{\ominus} < 0\,\text{kG}$, *weakly acidic*. This rough classification may be refined as shown in Table 7.2. Talking about strong or weak acids or bases instead of acid–base pairs is common practice,

Table 7.2 Classification of acid–base pairs in aqueous solution according to their acidic strength.

Ad/Bs may be called	For $\overset{\circ}{\mu}_{\text{p}}$(kG) in the range
Very strong acidic	$>+20$
Strong acidic	$0 \ldots +20$
Moderate acidic	$-20 \ldots 0$
Weak acidic	$-40 \ldots -20$
Weak alkaline	$-60 \ldots -40$
Moderate alkaline	$-80 \ldots -60$
Strong alkaline	$-100 \ldots -80$
Very strong alkaline	<-100

but not very opportune. The acidic or alkaline (basic) strength is a property of the pair as a whole and not only of a part of it. (To avoid any possibility of confusion with the term “basic value” (“basic” in the sense of “fundamental”) we will use only “alkaline” in the following.)

When two acid–base pairs are present in a solution, the “stronger acidic” pair forces protons upon the “weaker acidic” one. Because acid–base equilibrium occurs almost instantly, a uniform proton potential is established through the exchange of protons even when different acids and bases are present:

$$\begin{aligned}\mu_\mathrm{p} &= \mu_\mathrm{p}(\mathrm{Ad/Bs}) = \mu_\mathrm{p}(\mathrm{Ad^*/Bs^*}) \\ &= \ldots \qquad \text{(“Proton potential equalization”).} \end{aligned} \tag{7.2}$$

Equation (7.2) expresses an important fact: The proton potential μ_p represents a property of a chemical system which has a universal meaning comparable to that of pressure p and temperature T.

Strong Acid–Base Pairs In aqueous solutions, strong acidic pairs such as perchloric acid or hydrochloric acid almost completely lose their protons to the water (H_3O^+/H_2O pair). One might say they totally “dissociate,” for example

$$\mathrm{HClO_4|w + H_2O|l \rightarrow ClO_4^-|w + H_3O^+|w}$$

or

$$\mathrm{HCl|w + H_2O|l \rightarrow Cl^-|w + H_3O^+|w.}$$

In both cases, the acid of the weaker acidic pair (H_3O^+) replaces that of the stronger acidic one ($HClO_4$ or HCl, respectively). Since the deprotonation is almost complete, the same acid H_3O^+ is present in both cases and therefore the pair H_3O^+/H_2O with the highest possible acidic strength in not too concentrated aqueous solutions. In the process, the proton potential decreases from rather high and different positive values (+57 and +35 kG, respectively) to the same value of (just about) zero. Hence, strong acidic pairs cannot develop their full power in an aqueous solution. In this case, one speaks of the *leveling effect* of the solvent water. For this reason, the chemical potentials $\mu(\mathrm{Ad})$ of undissociated strong acids (which are necessary for determining individual proton potentials) are measured in nonaqueous solutions and the results transferred as approximations to the solvent water.

If one wishes to find the proton potential of a strong acidic pair at arbitrary dilution, it is enough to just consider the acid–base pair H_3O^+/H_2O:

$$\mu_\mathrm{p} = \mu_\mathrm{p}(\mathrm{H_3O^+/H_2O}) = \frac{1}{1}[\mu(\mathrm{H_3O^+}) - \mu(\mathrm{H_2O})].$$

When the concentrations are small, the mass action equation can be applied.

However, there is such an excess of water (the solvent) present that its concentration shows almost no change during the reaction. As stated, it can be treated as a pure liquid (compare Sect. 6.3):

$$\begin{aligned}\mu_\mathrm{p} &= \overset{\circ}{\mu}(\mathrm{H_3O^+}) + RT\ln c_\mathrm{r}(\mathrm{H_3O^+}) - \overset{\circ}{\mu}(\mathrm{H_2O}) \\ &= \left[\overset{\circ}{\mu}(\mathrm{H_3O^+}) - \overset{\circ}{\mu}(\mathrm{H_2O})\right] + RT\ln c_\mathrm{r}(\mathrm{H_3O^+}).\end{aligned}$$

The difference in parentheses corresponds to the basic value of the proton potential of the pair H_3O^+/H_2O, meaning

$$\mu_\mathrm{p} = \overset{\circ}{\mu}_\mathrm{p}(\mathrm{H_3O^+/H_2O}) + RT\ln c_\mathrm{r}(\mathrm{H_3O^+}). \tag{7.3}$$

If, for example, we are interested in the proton potential of hydrochloric acid with a concentration of 0.01 kmol $\mathrm{m^{-3}}$, the concentration of H_3O^+ corresponds to the stated HC1 concentration due to the total dissociation. If we continue to take into account that $\overset{\circ}{\mu}_\mathrm{p}(\mathrm{H_3O^+/H_2O}) = \mu_\mathrm{p}^{\ominus}(\mathrm{H_3O^+/H_2O}) = 0$ (compare Table 7.1), we obtain for 298 K (and 100 kPa):

$$\mu_\mathrm{p} = 0\ \mathrm{G} + 8.314\ \mathrm{G\,K^{-1}} \times 298\,\mathrm{K} \times \ln 0.01 = -11\,\mathrm{kG}.$$

The proton potential is noticeably smaller than the basic value which is valid for a H_3O^+ concentration of 1 kmol $\mathrm{m^{-3}}$ in an aqueous solution.

The bases of strong alkaline pairs $\left(\overset{\circ}{\mu}_\mathrm{p} < -80\,\mathrm{kG}\right)$, such as amide ions NH_2^-, suffer a similar fate where, due to the higher $\overset{\circ}{\mu}_\mathrm{p}$ value, the water (H_2O/OH^- pair) forces the protons upon them:

$$\mathrm{NH_2^-|w + H_2O|l \rightarrow NH_3|w + OH^-|w}.$$

The amide ion is a strong proton acceptor that is almost totally protonated when present in an excess of water. The concentration of the hereby produced base OH^- determines the proton potential μ_p, whereas the concentration and thus the chemical potential of its corresponding acid H_2O remains almost unaltered. In aqueous solutions of alkaline acid–base pairs, therefore, μ_p cannot fall far below −80 kG. Traditionally, this statement is expressed saying OH^- is the strongest base to be found in water.

Determining the proton potential of a dilute strong alkaline pair follows the same pattern as for a dilute strong acidic pair, although in this case, the pair H_2O/OH^- (instead of H_3O^+/H_2O) must be considered:

$$\mu_\mathrm{p} = \mu_\mathrm{p}(\mathrm{H_2O/OH^-}) = \frac{1}{1}[\mu(\mathrm{H_2O}) - \mu(\mathrm{OH^-})].$$

By taking into account the special situation of water as solvent as well as the mass action equation for OH^-, one obtains

$$\mu_\mathrm{p} = \overset{\circ}{\mu}(\mathrm{H_2O}) - \left[\overset{\circ}{\mu}(\mathrm{OH^-}) + RT\ln c_\mathrm{r}(\mathrm{OH^-})\right]$$

and finally

$$\mu_\mathrm{p} = \overset{\circ}{\mu}_\mathrm{p}(\mathrm{H_2O/OH^-}) - RT\ln c_\mathrm{r}(\mathrm{OH^-}). \tag{7.4}$$

Thus, at 298 K (and 100 kPa), a strong alkaline pair with a concentration of 0.1 kmol $\mathrm{m^{-3}}$ in water has a proton potential of

$$\mu_\mathrm{p} = -80 \times 10^3\,\mathrm{G} - 8.314\,\mathrm{G\,K^{-1}} \times 298\,\mathrm{K} \times \ln 0.1 = -74\,\mathrm{kG},$$

which is noticeably higher than the standard value of −80 kG.

A proton potential considerably lower than −80 kG cannot be maintained in normal aqueous solutions because the water would continuously decompose due to loss of protons. The same is true for a potential considerably above 0 kG because here the H_2O molecules are destroyed by the production of H_3O^+. In both cases, the water would largely disappear so that the term "aqueous solution" would no longer apply. Conditions of this type dominate in concentrated solutions of mineral acids or alkali hydroxides.

Weak Acid–Base Pairs Acids of a weak acidic pair such as acetic acid HAc, on the other hand, can be deprotonated to very different degrees in an aqueous solution. (As mentioned, Ac is used as abbreviation for the acetate group CH_3COO.) If the acid–base pair is largely deprotonated, its proton reservoir is just about empty. However, if it is hardly deprotonated, meaning almost fully protonated, the proton reservoir is almost full. If one wishes to calculate the proton potential of a weak acidic pair such as HAc/Ac^- in a diluted aqueous solution, due to the incomplete proton transfer to the pair H_3O^+/H_2O, both pairs must be taken into account according to

$$\mathrm{HAc|w + H_2O|l \rightleftarrows Ac^-|w + H_3O^+|w}.$$

We start with the following equation for "proton potential equalization,"

$$\mu_\mathrm{p} = \mu_\mathrm{p}(\mathrm{Ad/Bs}) = \mu_\mathrm{p}(\mathrm{H_3O^+/H_2O}),$$

a special case of Eq. (7.2). When the mass action equation is applied and the special situation of water as solvent is taken into account, the result is

$$\overset{\circ}{\mu}_{\mathrm{p}}(\mathrm{Ad/Bs}) + RT\ln c_{\mathrm{r}}(\mathrm{Ad}) - RT\ln c_{\mathrm{r}}(\mathrm{Bs})$$
$$= \overset{\circ}{\mu}_{\mathrm{p}}(\mathrm{H_3O^+/H_2O}) + RT\ln c_{\mathrm{r}}(\mathrm{H_3O^+}). \qquad (7.5)$$

It immediately follows from the conversion formula that the concentration of the base formed by the proton transfer from the acid to the water is equal to that of the resulting oxonium ions, $c_{\mathrm{r}}(\mathrm{Bs}) = c_{\mathrm{r}}(\mathrm{H_3O^+})$. If we furthermore assume that the acid of the weak acidic pair is only slightly dissociated, the undissociated portion $c_{\mathrm{r}}(\mathrm{Ad})$ can, in first approximation, be equated to the initial concentration c_0, $c_{\mathrm{r}}(\mathrm{Ad}) \approx c_{0,\mathrm{r}}$. When both terms are inserted into Eq. (7.5) and this equation is solved for $RT \ln c_{\mathrm{r}}(\mathrm{H_3O^+})$, we obtain

$$\overset{\circ}{\mu}_{\mathrm{p}}(\mathrm{Ad/Bs}) + RT\ln c_{0,\mathrm{r}} - RT\ln c_{\mathrm{r}}(\mathrm{H_3O^+}) = \overset{\circ}{\mu}_{\mathrm{p}}(\mathrm{H_3O^+/H_2O}) + RT\ln c_{\mathrm{r}}(\mathrm{H_3O^+})$$

and finally

$$RT\ln c_{\mathrm{r}}(\mathrm{H_3O^+}) = 1/2 \cdot \left[\overset{\circ}{\mu}_{\mathrm{p}}(\mathrm{Ad/Bs}) - \overset{\circ}{\mu}_{\mathrm{p}}(\mathrm{H_3O^+/H_2O}) + RT\ln c_{0,\mathrm{r}}\right].$$

Insertion of this term into Eq. (7.3) results in a relation for the proton potential:

$$\mu_{\mathrm{p}} = 1/2 \cdot \left[\overset{\circ}{\mu}_{\mathrm{p}}(\mathrm{Ad/Bs}) + \overset{\circ}{\mu}_{\mathrm{p}}(\mathrm{H_3O^+/H_2O}) + RT\ln c_{0,\mathrm{r}}\right]. \qquad (7.6)$$

According to this, the proton potential at 298 K (and 100 kPa) of an acetic acid solution with a concentration of 1 kmol m^{-3} is:

$$\mu_{\mathrm{p}} = 1/2 \times \left[\left(-27 \times 10^3\,\mathrm{G}\right) + 0 + 8.314\,\mathrm{G\,K^{-1}} \times 298\,\mathrm{K} \times \ln 1\right] = -13.5\,\mathrm{kG}.$$

This is noticeably higher than the standard value of −27 kG (see Table 7.1) and can be explained by the fact that the acetate concentration is negligibly small compared to the concentration of undissociated acetic acid. (On the other hand, the standard value is valid for a concentration ratio of $c(\mathrm{HAc}){:}c(\mathrm{Ac^-})$ of 1:1; compare Sect. 7.4.)

The proton potential of a weak alkaline pair in aqueous solution can be derived analogously. The result is comparable to Eq. (7.6):

$$\mu_{\mathrm{p}} = 1/2 \cdot \left[\overset{\circ}{\mu}_{\mathrm{p}}(\mathrm{Ad/Bs}) + \overset{\circ}{\mu}_{\mathrm{p}}(\mathrm{H_2O/OH^-}) - RT\ln c_{0,\mathrm{r}}\right]. \qquad (7.7)$$

Accordingly, a solution of ammonia in water with the corresponding conversion formula

$$\mathrm{NH_3|w + H_2O|l \rightleftarrows NH_4^+|w + OH^-|w}$$

has a proton potential of

$$\begin{aligned}\mu_\mathrm{p} &= ½ \times \left[\left(-53\times10^3\,\mathrm{G}\right) + \left(-80\times10^3\,\mathrm{G}\right) - 8.314\,\mathrm{G\,K^{-1}} \times 298\,\mathrm{K} \times \ln 0.1\right]\\ &= -64\,\mathrm{kG},\end{aligned}$$

when a concentration of 0.1 kmol m^{-3} at 298 K (and 100 kPa) is considered.

Acid–Base Disproportionation of Water Finally, we will take a look at the *acid–base disproportionation* of water. It has already been demonstrated that amphoteric water can function as an acid as well as a base. For this reason, proton transfer between the water molecules can take place where oxonium and hydroxide ions are formed even when there are no other acids or bases present:

$$\underbrace{\mathrm{H_2O|l}}_{\mathrm{Bs}} + \underbrace{\mathrm{H_2O|l}}_{\mathrm{Ad*}} \rightleftarrows \underbrace{\mathrm{H_3O^+|w}}_{\mathrm{Ad}} + \underbrace{\mathrm{OH^-|w}}_{\mathrm{Bs*}}.$$

The proton potential of the acid–base pair H_3O^+/H_2O results from Eq. (7.3) and that of the pair H_2O/OH^- from Eq.(7.4). Both potentials have to be equal in the same solution:

$$\mu_\mathrm{p} = \overset{\circ}{\mu}_\mathrm{p}(\mathrm{H_3O^+/H_2O}) + RT\ln c_\mathrm{r}(\mathrm{H_3O^+}) = \overset{\circ}{\mu}_\mathrm{p}(\mathrm{H_2O/OH^-}) - RT\ln c_\mathrm{r}(\mathrm{OH^-}).$$

Pure water is electrically neutral, so the H_3O^+ concentration must be equal to the OH^- concentration. Replacing $c_\mathrm{r}(\mathrm{OH^-})$ by $c_\mathrm{r}(\mathrm{H_3O^+})$ and solving the last equation for $c(\mathrm{H_3O^+}) = c^\ominus \cdot c_r(\mathrm{H_3O^+})$ yields

$$c(\mathrm{H_3O^+}) = c^\ominus \cdot \exp\frac{\overset{\circ}{\mu}_\mathrm{p}(\mathrm{H_2O/OH^-}) - \overset{\circ}{\mu}_\mathrm{p}(\mathrm{H_3O^+/H_2O})}{2RT}.$$

Taking the standard values in Table 7.1 at 298 K (and 100 kPa) results in

$$c(\mathrm{H_3O^+}) = 1\,\mathrm{kmol\,m^{-3}} \times \exp\frac{-80\times10^3\,\mathrm{G} - 0\,\mathrm{G}}{2\times 8.314\,\mathrm{G\,K^{-1}} \times 298\,\mathrm{K}} = 10^{-7}\,\mathrm{kmol\,m^{-3}}.$$

If this concentration is inserted into Eq. (7.3), one obtains the corresponding proton potential. This is −40 kG and is called the *neutral value*. An aqueous solution with a proton potential above −40 kG is called acidic; one with a proton potential under −40 kG is called alkaline (basic).

Relationship to Other Measures of Acidity In closing, we will take a look at how the proton potential relates to other common measures used for acidity. There is a close relationship between the standard value of the proton potential $\mu_p^\ominus$ (Ad/Bs) of an acid–base pair [more generally stated, its basic value $\overset{\circ}{\mu}_p(\mathrm{Ad/Bs})$], and the acidity exponent or pK value. For this purpose, we will look again at proton transfer equilibrium,

$$\mathrm{HA|w + H_2O|l \rightleftarrows A^-|w + H_3O^+|w},$$

where HA corresponds to an acid Ad and $\mathrm{A^-}$ to a base Bs. Equation (7.5) can be converted to

$$\overset{\circ}{\mu}_p(\mathrm{Ad/Bs}) - \overset{\circ}{\mu}_p(\mathrm{H_3O^+/H_2O}) = RT\ln\frac{c_r(\mathrm{Bs})\cdot c_r(\mathrm{H_3O^+})}{c_r(\mathrm{Ad})}. \tag{7.8}$$

As already stated, we have $\overset{\circ}{\mu}_p(\mathrm{H_3O^+/H_2O}) = 0$ (at standard pressure) for the proton potential. It represents the "reference level," so to speak.

The equilibrium "constants" of the reaction (see Sect. 6.4),

$$\overset{\circ}{\mathcal{K}}_a(\mathrm{Ad/Bs}) = \frac{c_r(\mathrm{Bs})\cdot c_r(\mathrm{H_3O^+})}{c_r(\mathrm{Ad})} \quad \text{and} \quad \overset{\circ}{K}_a(\mathrm{Ad/Bs}) = \frac{c(\mathrm{Bs})\cdot c(\mathrm{H_3O^+})}{c(\mathrm{Ad})},$$

are both called *acidity constants*. Adding Ad/Bs as argument behind $\overset{\circ}{\mathcal{K}}_a$ and $\overset{\circ}{K}_a$ would be more elucidative, but is quite uncommon. If it is clear from the context which pair is meant or if the kind of pair does not matter we will in the future omit the argument Ad/Bs. These constants can vary by many orders of magnitude depending upon the chemical structure of the acids or bases. Therefore it is useful to introduce a logarithmic scale. Generally, one uses the negative decadic logarithm (logarithm to base 10) of the acidity constant, the acidity exponent or *pK_a value* (or simply the *pK value*):

$$\mathrm{p}K_a = -\lg\overset{\circ}{\mathcal{K}}_a.$$

In this case, the numerical acidity constant $\overset{\circ}{\mathcal{K}}_a$ needs to be used instead of the conventional $\overset{\circ}{K}_a$ because the argument of the logarithm must be a number.

If we convert the natural logarithm to decadic logarithm in Eq. (7.8), by using $\ln x = \ln 10 \cdot \lg x$ [Eq. (A.1.5) in the Appendix], we obtain

$$\overset{\circ}{\mu}_{\mathrm{p}} = -RT\ln 10 \cdot \mathrm{p}K_{\mathrm{a}}.$$

The term $RT\ln 10$ corresponds to the decapotential μ_{d} (compare to Sect. 6.2), meaning that

$$\overset{\circ}{\mu}_{\mathrm{p}} = -\mu_{\mathrm{d}} \cdot \mathrm{p}K_{\mathrm{a}}. \tag{7.9}$$

In general, the basic value $\overset{\circ}{\mu}_{\mathrm{p}}(\mathrm{Ad}/\mathrm{Bs})$ of the proton potential and the $\mathrm{p}K_{\mathrm{a}}$ value are proportional. If we place the acids in a sequence according to their strength, we get the same result independent of which of the two measures is being used.

A very similar looking equation relates the proton potential μ_{p} in the solution after proton potential equalization to the so-called hydrogen ion exponent or *pH value* that represents a special measure of acidity expressed by the H_3O^+/H_2O pair. We should call to mind that μ_{p} in a homogeneous solution has the same value for all acid–base pairs present [Eq. (7.2)]. Which pair one uses for measuring μ_{p} is not essential. The term pH value (derived from the Latin "pondus hydrogenii," meaning as much as "weight of hydrogen") was introduced by the Danish scientist Søren Peder Lauritz Sørensen in 1909. Originally, it was the "exponent of the power to the base 10" of the "concentration of hydrogen ions in water, measured in mol/L," $\{c(\mathrm{H}^+|\mathrm{w})\}_{\mathrm{mol/L}}$. The negative sign in the exponent was dropped. The curly brackets signify that it is a pure numerical value. This means if we omit the supplement "|w" for the sake of simplicity:

$$\{c(\mathrm{H}^+)\}_{\mathrm{mol/L}} = 10^{-\,\mathrm{pH}} \quad \text{or} \quad c(\mathrm{H}^+)/c^{\ominus} = 10^{-\,\mathrm{pH}}.$$

The pH value as negative decadic logarithm of the relative concentration of (hydrated) hydrogen ions or, more exactly, (hydrated) oxonium ions—H^+, $\mathrm{H}^+|\mathrm{w}$, $\mathrm{H_3O}^+$, $\mathrm{H_3O}^+|\mathrm{w}$ are here only different notations for the same kind of particles!—

$$\mathrm{pH} := -\lg\frac{c(\mathrm{H}^+)}{c^{\ominus}} = -\lg c_{\mathrm{r}}(\mathrm{H}^+) \quad \text{or} \quad \mathrm{pH} := -\lg\frac{c(\mathrm{H_3O}^+)}{c^{\ominus}} = -\lg c_{\mathrm{r}}(\mathrm{H_3O}^+)$$

represents (as does the pK value) a handier numerical value because the concentrations can vary by many orders of magnitude. For reasons of convenience, the specification $\{\,\}_{\mathrm{mol/L}}$ or $c^{\ominus}$ is generally dropped. However, this can easily lead to errors when other units of concentration are also being used and should, for this reason, be avoided.

Sørensen's equation can be contrasted with the proton potential μ_{p} of Eq. (7.3),

$$\mu_{\mathrm{p}} = \overset{\circ}{\mu}_{\mathrm{p}}(\mathrm{H_3O}^+/\mathrm{H_2O}) + RT\ln c_{\mathrm{r}}(\mathrm{H_3O}^+).$$

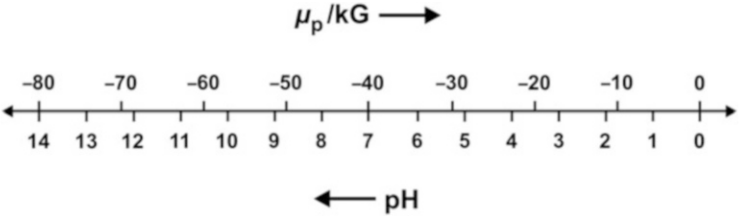


Fig. 7.1 Relation between proton potential μ_p and pH value in an aqueous solution at 298 K and 100 kPa.

$c_r(H_3O^+)$ is the (relative) concentration of oxonium ions that is reached after proton potential equalization. We again observe that $\overset{\circ}{\mu}_p(H_3O^+/H_2O) = 0$ (at standard pressure) and convert the natural into the decadic logarithm. We find

$$\mu_p = -RT\ln 10 \cdot \text{pH}$$

or finally because of $RT \ln 10 = \mu_d$

$$\mu_p = -\mu_d \cdot \text{pH}. \tag{7.10}$$

This is a simple but important result.

According to Sørensen's definition, this relation is only valid for small concentrations c. These days, however, the pH value is defined so that this equation is *always* valid. Figure 7.1 clarifies the relation between proton potential μ_p and pH value in an aqueous solution at 298 K.

The pH value is just a variation of proton potential—in other words μ_p in a specialized scale. Differences of pH values ultimately mean differences in chemical potential and therefore, differences in the drive of the chemical reactions in which the protons take part.

In matter dynamics, the description of the proton potential μ_p as a measure of the strength of an acid–base pair that we have just been introduced to offers several advantages not present in conventional measures of acidity (pK and pH values):

- At the conceptual level, acid–base reactions and other transfer reactions, especially redox reactions, can be treated uniformly (cf. Sect. 22.4).
- Strengths of acids and numerical values of the measure of acidity run parallel (and do not, as with pK values, run opposite to each other).
- The proton potential also indicates the strength of an acid–base pair with respect to the concentration dependence (the pK value as a logarithm of an equilibrium constant cannot do this, so that in this case, another measure, the pH value is used instead).

7.4 Level Equation and Protonation Equation

Monoprotic Acid–Base Pairs The extent of protonation of an acid–base pair, briefly its “fill level,” can be described by the *degree of protonation* Θ. In the case of a monoprotic pair, this is understood to be the portion of base molecules that are protonated in relation to the total concentration of acid and base molecules:

$$\Theta = \frac{c_{\mathrm{Ad}}}{c_{\mathrm{Bs}} + c_{\mathrm{Ad}}}. \tag{7.11}$$

The degree of protonation depends upon the proton potential μ_{p} in the solution. Based upon the condition of equilibrium, $\mu_{\mathrm{p}} = \frac{1}{1}[\mu_{\mathrm{Ad}} - \mu_{\mathrm{Bs}}]$, and the mass action equation,

$$\mu_{\mathrm{p}} = \left(\overset{\circ}{\mu}_{\mathrm{Ad}} + RT\ln(c_{\mathrm{Ad}}/c^{\ominus})\right) - \left(\overset{\circ}{\mu}_{\mathrm{Bs}} + RT\ln(c_{\mathrm{Bs}}/c^{\ominus})\right)$$

one obtains a relation that corresponds to the Henderson–Hasselbalch equation ($\mathrm{pH} = \mathrm{p}K_{\mathrm{a}} + \log(c_{\mathrm{Bs}}/c_{\mathrm{Ad}})$),

$$\mu_{\mathrm{p}} = \overset{\circ}{\mu}_{\mathrm{p}} + RT\ln\frac{c_{\mathrm{Ad}}}{c_{\mathrm{Bs}}} \quad (\text{“Level equation”}), \tag{7.12}$$

where μ_{p} represents the hydrogen ion exponent or pH value, and $\overset{\circ}{\mu}_{\mathrm{p}}$ stands for the acidity exponent or pK_{a} value. This is the so-called level equation. The name comes from the fact that μ_{p} describes how high the “acidity level” is in the Ad/Bs reservoir, or in other words, how strongly acidic the Ad/Bs pair reacts.

The quotient $c_{\mathrm{Ad}}/c_{\mathrm{Bs}}$ can be expressed using the degree of protonation Θ so that we have

$$\mu_{\mathrm{p}} = \overset{\circ}{\mu}_{\mathrm{p}} + RT\ln\frac{\Theta}{1-\Theta}. \tag{7.13}$$

According to Eq. (7.11) we have

$$\Theta(c_{\mathrm{Bs}} + c_{\mathrm{Ad}}) = c_{\mathrm{Ad}} \text{ or } \Theta \cdot c_{\mathrm{Bs}} = (1-\Theta) \cdot c_{\mathrm{Ad}}$$

and finally

$$c_{\mathrm{Ad}}/c_{\mathrm{Bs}} = \Theta/(1-\Theta).$$

$\overset{\circ}{\mu}_{\mathrm{p}}$ vividly represents the "half-potential," meaning the proton potential present at a degree of protonation equal to $\Theta = ½$. This is when the concentrations of acid and base are equal. In the case of $\mu_{\mathrm{p}} > \overset{\circ}{\mu}_{\mathrm{p}}$, the acid–base pair is present mostly in the protonated form, and for $\mu_{\mathrm{p}} < \overset{\circ}{\mu}_{\mathrm{p}}$ it is primarily present in the deprotonated form.

When the relation (7.13) is solved for Θ, the following equation results:

$$\Theta = \frac{1}{1 + \exp\dfrac{\overset{\circ}{\mu}_{\mathrm{p}} - \mu_{\mathrm{p}}}{RT}} \qquad \text{("Protonation equation")}, \tag{7.14}$$

which we will encounter repeatedly in a similar form.

We transform Eq. (7.13) into

$$\frac{\Theta}{1-\Theta} = \exp\frac{\mu_{\mathrm{p}} - \overset{\circ}{\mu}_{\mathrm{p}}}{RT} = a.$$

With the abbreviation a and two intermediate steps,

$$a^{-1} = \frac{1-\Theta}{\Theta} = \Theta^{-1} - 1 \ \text{ and } \ \Theta = \frac{1}{1+a^{-1}},$$

we obtain Eq. (7.14).

Figure 7.2 graphically presents the relation $\Theta = f(\mu_{\mathrm{p}})$ described by the protonation equation (7.14). It shows that the curves of different monoprotic acid–base pairs have the same form. They are simply shifted along the μ_{p} axis.

Taking this aspect into account, let us reconsider our examples from Sect. 7.2. We had determined a proton potential of −13.5 kG for an aqueous solution of acetic acid with a concentration of 1 kmol m^{-3}. Inserting this into the protonation

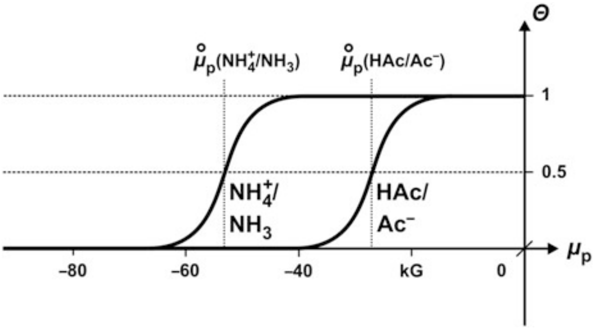


Fig. 7.2 Degree of protonation Θ of the acid–base pairs HAc/Ac$^-$ and NH_4^+/NH_3 at 298 K (and 100 kPa), as a function of the proton potential μ_{p}.

equation, and using the standard value of $\mu_{\mathrm{p}}^{\ominus}(\mathrm{HAc}/\mathrm{Ac}^-) = -27$ kG at 298 K (and 100 kPa), yields a degree of protonation of

$$\Theta = \frac{1}{1 + \exp\dfrac{-27 \times 10^3\,\mathrm{G} - \left(-13.5 \times 10^3\,\mathrm{G}\right)}{8.314\,\mathrm{G\,K^{-1}} \times 298\,\mathrm{K}}} = 0.996.$$

This means that 99.6 % of the amount of acid used exists in protonated form (in the form of acetic acid molecules). Only 0.4 % exists in deprotonated form as acetate ions. Our original assumption that acids of weak acidic acid–base pairs are present in dissociated form only to a very small proportion is therefore justified. (This is the case as long as the dissociated fraction remains smaller than about 5 %; since the degree of protonation is also dependent upon the initial concentration of c_0, via μ_{p}, the validity of the simplification must be ascertained from case to case.)

We can proceed analogously for an ammonia solution with a concentration of 0.1 kmol m^{-3} and obtain a degree of protonation of 0.012. This means only 1.2 % of the ammonia molecules have been protonated.

Let us return once again to our image of acid–base pairs as reservoirs for protons. We can consider the degree of protonation to be the relation of the amount of protons n_{p} in the reservoir to the maximum amount of protons $n_{\mathrm{p,max}}$ that can be stored:

$$\Theta = \frac{n_{\mathrm{p}}}{n_{\mathrm{p,\,max}}}. \tag{7.15}$$

When this expression is inserted into Eq. (7.14) and solved for n_{p}, we obtain a variation of the protonation equation:

$$n_{\mathrm{p}} = \frac{n_{\mathrm{p,\,max}}}{1 + \exp\dfrac{\overset{\circ}{\mu}_{\mathrm{p}} - \mu_{\mathrm{p}}}{RT}}. \tag{7.16}$$

The protonation equation quasi shows the "fill level" in the proton reservoir. The graphic representation corresponds to Fig. 7.2, just that the curve approaches $n_{\mathrm{p,max}}$ instead of a value of 1.

Water as a Special Case Let us now consider a special case of the acid–base pairs where the solvent water is the reaction partner and where the pairs limit the range of potentials of the weakly and moderately acidic and alkaline pairs from that of the strong ones. For the acid–base pair H_3O^+/H_2O with $\overset{\circ}{\mu}_\mathrm{p}(H_3O^+/H_2O) = 0$ (at standard pressure), we obtain a level equation corresponding to Eq. (7.3):

$$\mu_\mathrm{p} = \overset{\circ}{\mu}_\mathrm{p}(H_3O^+/H_2O) + RT\ln c_\mathrm{r}(H_3O^+).$$

If we replace the relative concentration in this equation by the following expression:

$$c_\mathrm{r}(H_3O^+) = \frac{c(H_3O^+)}{c^\ominus} = \frac{n(H_3O^+)}{V \cdot c^\ominus} = \frac{n_\mathrm{p}}{V \cdot c^\ominus},$$

and solve for n_p, the corresponding protonation equation results:

$$n_\mathrm{p} = V \cdot c^\ominus \cdot \exp\left(-\frac{\overset{\circ}{\mu}_\mathrm{p}(H_3O^+/H_2O) - \mu_\mathrm{p}}{RT}\right). \qquad (7.17)$$

According to Eq. (7.4), the level equation for the pair H_2O/OH^-, with $\overset{\circ}{\mu}_\mathrm{p}(H_2O/OH^-) = -80\,\mathrm{kG}$, is:

$$\mu_\mathrm{p} = \overset{\circ}{\mu}_\mathrm{p}(H_2O/OH^-) - RT\ln c_\mathrm{r}(OH^-).$$

It is now possible to describe the deprotonation of water as a deficit of protons, meaning it can be described by negative n_p values:

$$c_\mathrm{r}(OH^-) = \frac{c(OH^-)}{c^\ominus} = \frac{n(OH^-)}{V \cdot c^\ominus} = \frac{-n_\mathrm{p}}{V \cdot c^\ominus}.$$

By inserting the result in the equation above and solving for n_p, we obtain for the protonation equation

$$n_\mathrm{p} = -V \cdot c^\ominus \cdot \exp\left(+\frac{\overset{\circ}{\mu}_\mathrm{p}(H_2O/OH^-) - \mu_\mathrm{p}}{RT}\right). \qquad (7.18)$$

If there are several acid–base pairs Ad/Bs, Ad*/Bs*, … in a solution, the amounts of protons in the individual reservoirs add up to a total “fill amount” $n_\mathrm{p,total}$:

$$n_\mathrm{p,total} = n_\mathrm{p}(\mathrm{Ad/Bs}) + n_\mathrm{p}(\mathrm{Ad^*/Bs^*}) + \ldots . \qquad (7.19)$$

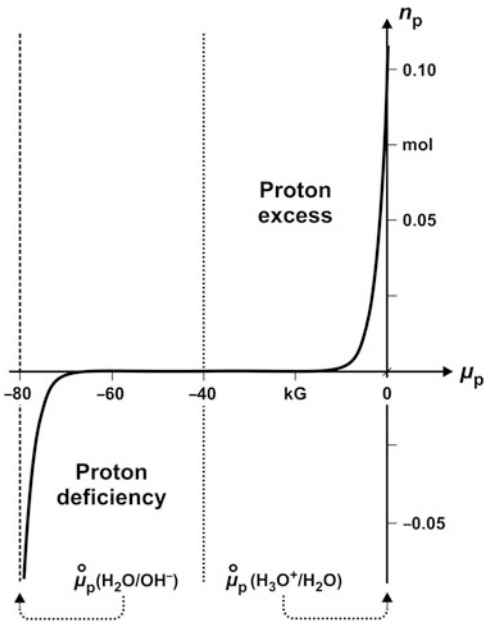


Fig. 7.3 Total amount $n_{p,total}$ in the storage medium water as a function of the proton potential μ_p in a volume of 100 mL at 298 K.

In the case of water, the pairs H_3O^+/H_2O and H_2O/OH^- must be taken into account due to the amphoteric character of the water. The resulting total amount is

$$n_{p,\text{total}} = n_p(H_3O^+/H_2O) + n_p(H_2O/OH^-).$$

If pure water is considered, the slight amount of protons that appear due to disproportionation is compensated for by the lack of protons so that the total "fill amount" equals zero. Figure 7.3 shows the cumulative curve that combines the two branches of the curve described by Eqs. (7.17) and (7.18).

How can the "fill level" in the proton reservoir—as a function of the proton potential—be determined in the case of a weak acid–base pair dissolved in water? For this, the contribution of the pair in question and that of the water add up to a total curve (Fig. 7.4).

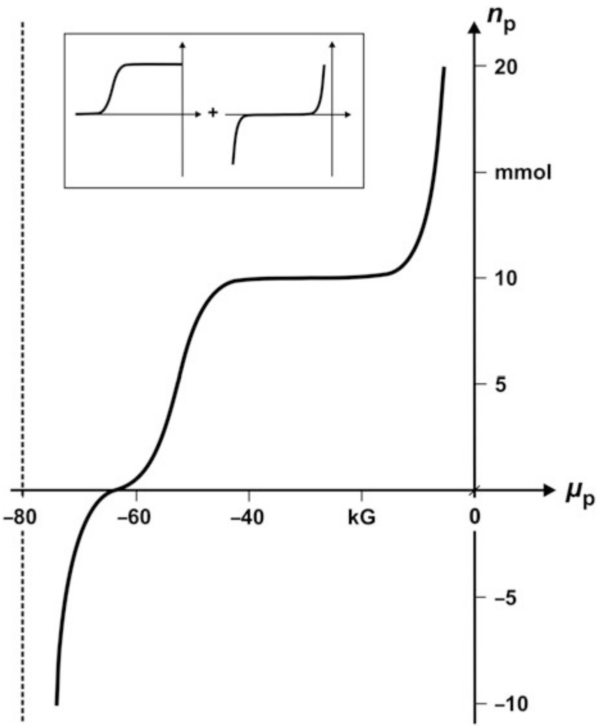


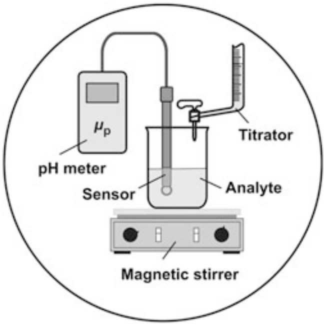
Fig. 7.4 "Fill level" of the protons as a function of proton potential for an aqueous solution of a monoprotic acid–base pair using the example NH_4^+/NH_3 (10 mmol in 100 mL solution) at 298 K.

7.5 Acid–Base Titrations

An important application for acid–base equilibria is the analytic method called *titration*. With the help of titration, it is possible to investigate the composition of an initial solution using the *equivalence point*. Moreover, it can also be used to determine the basic value $\overset{\circ}{\mu}_p(\mathrm{Ad/Bs})$ for various acid–base pairs. In order to do this, a solution of precisely known concentration, the so-called *titrator* (titrant), is added successively from a burette to the *analyte* (titrand), the solution with unknown concentration being titrated, while the pH value is continuously measured. The proton potential μ_p is then determined from this data (Experiment 7.2). Data can be collected on a computer and directly processed. In a further development of titration, the addition of the titration solution can be automatically controlled.

If the proton potential is plotted as a function of the added volume of the titrator (or any other quantity dependent upon the added amount, such as the amount of protons), one obtains a so-called *titration curve*.

Experiment 7.2 *Acid–base titration*: One possibility would be for example the titration of a sodium hydroxide solution with hydrochloric acid. A suitable sensor for these and other aqueous solutions would be a glass electrode that will be discussed in more detail in Sect. 22.7.



To begin with, let us consider the titration of the base of a strong alkaline pair with the acid of a strong acidic pair, for example, the titration of 100 mL of sodium hydroxide solution ($c(\text{NaOH}) = 0.1\ \text{kmol m}^{-3}$) with hydrochloric acid ($c(\text{HCl}) = 1\ \text{kmol m}^{-3}$). Sodium hydroxide in an aqueous solution is almost totally dissociated, so the behavior of the solution being titrated is determined by the pair H_2O/OH^-. At 298 K (and 100 kPa), the proton potential of the initial solution is −74 kG. This was already calculated in Sect. 7.3 using Eq. (7.4) which generally holds for strong bases of this concentration. In the hydrochloric acid solution, however, the proton potential is determined by the pair H_3O^+/H_2O. The original proton deficit of $n_p = -0.1\ \text{kmol m}^{-3} \times 0.1 \times 10^{-3}\ \text{m}^3 = -0.01\ \text{mol} = -10\ \text{mmol}$ is depleted by 1 mmol per mL of added hydrochloric acid. If the titrator is present in a much higher concentration than the substance in the solution to be titrated, the increase of water due to the inflowing titration solution can be ignored. When titrating bases of strong alkaline pairs with acids of strong acidic pairs, generally only the pairs H_2O/OH^- and H_3O^+/H_2O have to be considered independent of the kind of strong acid–base pairs used (because of the leveling effect of the solvent water discussed in Sect. 7.3). The progress of titration results from the curve showing the total amount of protons in the storage medium water for a given volume of 100 mL (Fig. 7.3); or rather, it results from a section of this representation specified by the test conditions (Fig. 7.5a). At the beginning of titration, we have the pure sodium hydroxide solution (black point). As more hydrochloric acid is added, one moves in the direction of the arrow along the curve. If the proton potential is plotted as a function of the amount of protons added, the result is the corresponding titration curve (Fig. 7.5b).

At first, the proton potential changes only slightly as titrator is continuously added. However, as the point is approached where a stoichiometrically equivalent amount of hydrochloric acid (in this case 10 mmol) has been added to the sodium hydroxide solution, a drastic increase of proton potential occurs. At the *equivalence point*, there is no proton deficiency anymore, and the proton reservoir is completely filled. There is only an aqueous solution of Na^+ and Cl^- ions that has almost no influence upon the proton potential which is then equal to the neutral value of −40 kG of pure water. If we continue to add hydrochloric acid to the neutralized

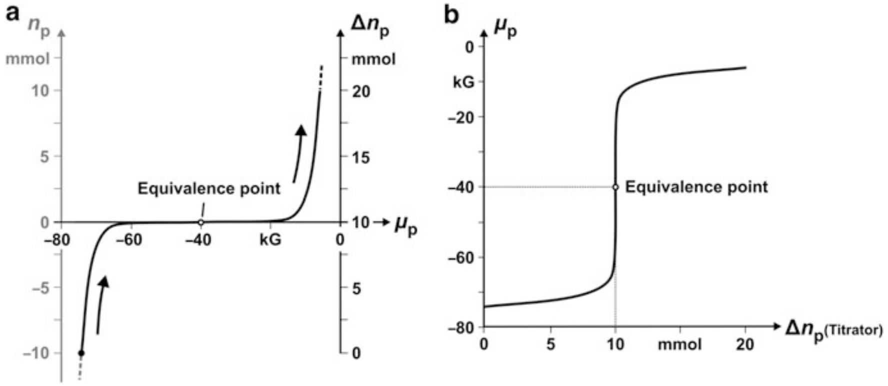


Fig. 7.5 (**a**) Total amount of protons $n_{p,\text{total}}$ in 100 mL water as a function of the proton potential μ_p, at 298 K, assuming a proton deficit of -10 mmol (black point), (**b**) Corresponding titration curve.

solution, the protons cannot be stored in the proton reservoir H_2O/OH^- already completely filled and the acid–base pair H_3O^+/H_2O of the titrator system determines the proton potential. Beyond the equivalence point, the increase of the proton potential is initially steep but starts leveling off very quickly.

Let us now turn to the titration of the base of a weak alkaline pair with the acid of a strong acidic pair using the example of titration of 100 mL of a 0.1 M ammonia solution with the standard solution of hydrochloric acid already used above. At first, the proton potential is -64 kG, which we have already calculated in Sect. 7.3 with the help of Eq. (7.7). The very low proton "fill level" of 1.2 % in the reservoir NH_4^+/NH_3 is just compensated for by the proton deficiency (which is caused by the OH^- ions produced by the proton transfer according to $NH_3 + H_2O \rightleftarrows NH_4^+ + OH^-$) so that the total "fill level" in the aqueous solution equals zero. The relation in Fig. 7.4, or more exactly, a section of it (Fig. 7.6a), is now what determines the form of the titration curve.

As hydrochloric acid continues to be added, we again move in the direction of the arrows along the curve. In the beginning, the form of the curve is determined by the acid–base pair NH_4^+/NH_3 and the corresponding protonation equation, meaning it is essentially this proton reservoir which is filled up. Halfway to the equivalence point (when half of the maximum amount of protons the pair can store have been added) the proton potential reaches the basic value of $\overset{\circ}{\mu}_p\left(NH_4^+/NH_3\right) = -53\,\text{kG}$. The fractions of base (NH_3) and corresponding acid $\left(NH_4^+\right)$ are now equal and the reservoir is just half full. Before this point, the pair appears primarily in deprotonated form and, afterward, in the protonated form. At the equivalence point, exactly as many protons are added with the standard solution so that the entire base is protonated. This means that it has completely transformed into its corresponding acid (except from some traces). At this point, we have an aqueous solution of an acid that has the same concentration as the original base. For this

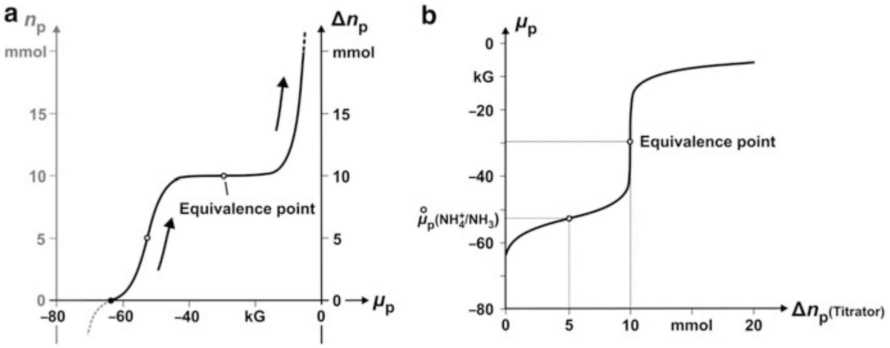


Fig. 7.6 (**a**) "Fill level" of the proton reservoir as a function of the proton potential for an aqueous solution of the acid–base pair NH_4^+/NH_3 (10 mmol in 100 mL solution) at 298 K, (**b**) Corresponding titration curve of an ammonia solution of equivalent concentration with the acid of a strong acidic pair.

reason we expect a proton potential that lies noticeably above the neutral point. It can be calculated according to Eq. (7.6) (the $C1^-$ ions that are also present have almost no influence upon the proton potential):

$$\mu_p = \tfrac{1}{2} \times \left(-53 \times 10^3\,\mathrm{G}\right) + \tfrac{1}{2} \times 0\,\mathrm{G} + \tfrac{1}{2} \times 8.314\,\mathrm{G\,K^{-1}} \times 298\,\mathrm{K} \times \ln 0.1$$
$$= -29\,\mathrm{kG}.$$

With continued addition of acid, the form of the curve is now determined by the acid–base pair H_3O^+/H_2O of the titrator system.

Figure 7.6b shows the corresponding titration curve. It is striking that after a small initial rise, the proton potential changes only very slowly until shortly before the equivalence point. We will go into the great importance of this fact in the next section. It also becomes clear that the basic value $\overset{\circ}{\mu}_p$ of a weak acid–base pair can be determined from the measured data by just reading the potential value halfway to the equivalence point. Again, the equivalence point makes itself felt by a sudden change of proton potential, just like it does in titration of exclusively strong acid–base pairs (but now it is less pronounced).

The changes of potential value in the titration of the acid of a weak acidic pair (e.g., acetic acid) with the base of a strong alkaline pair (such as sodium hydroxide solution) proceed similarly in principle and can be derived analogously. Again, the starting point for consideration is the "fill level" for an aqueous solution of an acid–base pair. The example used here is the pair HAc/Ac^- (10 mmol in 100 mL solution). At first, the acetic acid is almost fully protonated. The slight amount that is deprotonated is just compensated for by the H^+ ions that are produced so that the total "fill level" equals 10 mmol (Fig. 7.7a, black point). Adding sodium hydroxide solution slowly empties the proton reservoir and one moves in the direction of the arrow along the curve. At the equivalence point, a solution of the base of the weak alkaline pair is present in the deprotonated form of Ac^-. The corresponding proton potential shows a value noticeably below the neutral value.

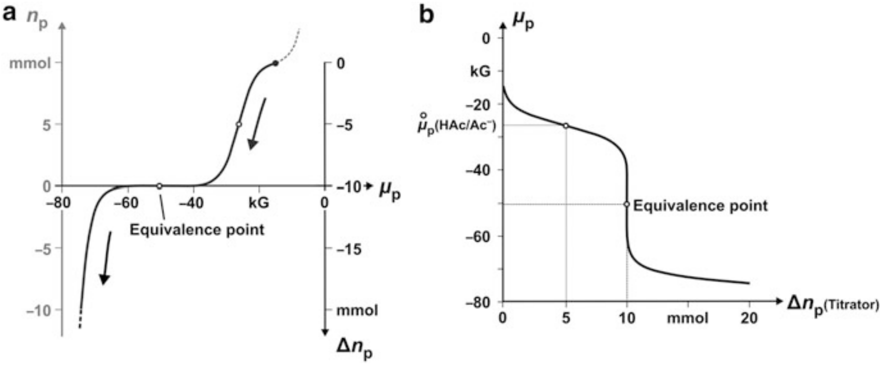


Fig. 7.7 (**a**) "Fill level" of a proton reservoir as a function of the proton potential for an aqueous solution of the acid–base pair HAc/Ac^- (10 mmol in 100 mL solution) at 298 K, (**b**) Corresponding titration curve of an acetic acid solution of equivalent concentration with the base of a strong alkaline pair.

Subsequently, the pair H_2O/OH^- determines the shape of the function. Figure 7.7b shows the corresponding titration curve.

If, however, the titrated system and the titrator are present in comparable concentrations, the initial approximation is no longer valid and the increase of the amount of water in the process of titration can no longer be ignored. The titration curve must then be calculated point for point by inserting the changing concentrations, which result from each addition of titrator, into the above relations. This is a lot of work. Since the basic form of the curves does not change much, however, we will leave it at a general understanding accepting the limitations mentioned.

7.6 Buffers

When a weak pair composed of approximately equal but large amounts of acid and its corresponding base is present in a solution, this pair determines the proton potential. Acids of weaker acidic pairs which are added cannot have any effect upon μ_p anyway (if we disregard effects of dilution, etc.), whereas acids of stronger acidic pairs—as long as they are at a shortfall—are robbed of their protons and so become ineffective. The same holds for adding a base. Our acid–base pair can absorb or *buffer* small outside disturbances without considerably changing μ_p of the solution. Hence, a solution in which μ_p reacts insensitively to the addition of slight amounts of acids or bases is called a *buffer*. Only when the acid of a stronger acidic pair is added to excess, for example, can the now almost totally protonated base no longer hinder the buildup of a higher proton potential. As a result, μ_p climbs to the value corresponding to the stronger acid–base pair.

The best way to show how a buffer works is in a potential diagram. Similar to matter capacity (see Sect. 6.7), we can introduce the *buffer capacity* B_p,

$$B_{\mathrm{p}} = \frac{\mathrm{d}n_{\mathrm{p}}}{\mathrm{d}\mu_{\mathrm{p}}},$$

by taking the derivative of the protonation equation (7.16) with respect to the proton potential μ_{p}. The corresponding result

$$B_{\mathrm{p}} = \frac{n_{\mathrm{p,\,max}}}{2RT \cdot \left(1 + \cosh\dfrac{\overset{\circ}{\mu}_{\mathrm{p}} - \mu_{\mathrm{p}}}{RT}\right)} \tag{7.20}$$

is not complicated but unfamiliar. The function cosh x is the so-called *hyperbolic cosine* whose values are simply the mean values of e^{x} and e^{-x}: $\cosh x = (\mathrm{e}^{x} + \mathrm{e}^{-x})/2$. Of course, we can directly insert the expression $(\mathrm{e}^{x} + \mathrm{e}^{-x})/2$ into Eq. (7.20), but the relation then appears less clearly.

We will make do with a qualitative discussion of the form of the function (Fig. 7.8a). At the point of inflection on the curve described by the protonation equation (7.16) (the point where the proton potential corresponds to the basic value $\overset{\circ}{\mu}_{\mathrm{p}}$ of the acid–base pair), the function $B_{\mathrm{p}}(n_{\mathrm{p}})$, being the derivative of the protonation equation, has, as expected, an extremum or, more precisely, a maximum value. As described in Sect. 6.7, the function of a buffer becomes even clearer when the axes are exchanged, $\sqrt{B/\pi}$ is calculated, and the curve is interpreted as the outline of a rotationally symmetric container (Fig. 7.8b). In contrast to the "exponential horn" that we have already seen, this container is rounded in form with the widest part in the area of the proton potential $\mu_{\mathrm{p}} = \overset{\circ}{\mu}_{\mathrm{p}}(\mathrm{Ad/Bs})$. If protons are added to the "reservoir" formed by the acid–base system, the "level" along with the proton potential changes very little in the range of the "wide-bellied container."

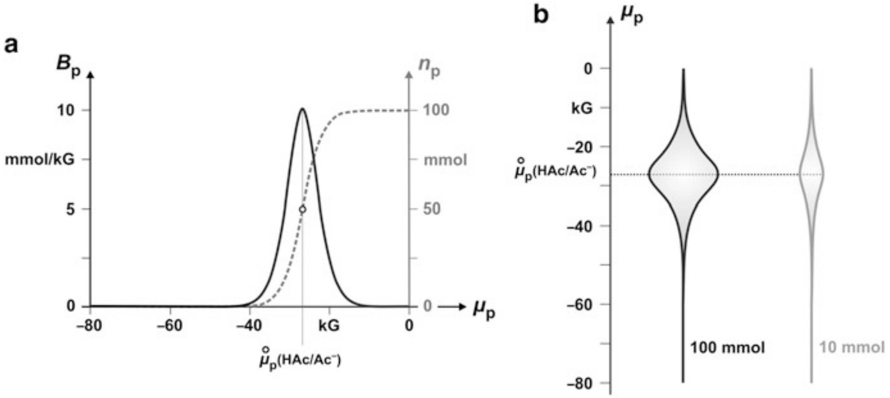


Fig. 7.8 (**a**) Plot of the stored amount of protons n_{p} (*gray dotted line*) and the corresponding buffer capacity B_{p} (*black continuous line*) as a function of proton potential μ_{p} at 298 K, using the example of the acid–base pair HAc/Ac^{-} (100 mmol), (**b**) Potential diagram of the buffer HAc/Ac^{-} for various total amounts of substance, $n = n(\mathrm{HAc}) + n(\mathrm{Ac}^{-})$.

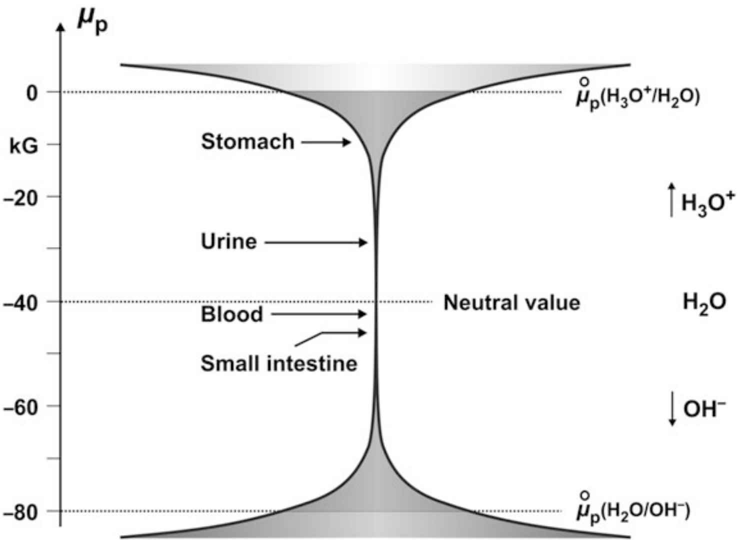


Fig. 7.9 Potential diagram for protons in water (by way of illustration, the proton potentials are shown in some bodily fluids).

The change of level is smaller the closer one gets to the most rounded out area of the container. Correspondingly, large amounts of protons can be added when the reservoir is only half full without the proton potential changing noticeably. The "proton reservoir" has the greatest capacity at this point. The size of the "proton reservoir" is determined by the total amount of substance $\mu_\mathrm{p,max}$; the greater the total amount of substance, the greater the buffer capacity. The size and shape of the "container" is the same for all acid–base pairs when the amount of substance remains the same. Only the position of the "container" shifts relative to the μ_p axis.

In the case of water, things look very different (Fig. 7.9). Within the range of $\mu_\mathrm{p} = -20\ldots-60$ kG, water has only a very small buffer capacity B_p or buffer capacity density $ϐ_\mathrm{p} = B_\mathrm{p}/V$, so that even tiny amounts of protons going into or out of a water sample can strongly change its proton potential. Starting from the neutral point, the amount of protons bound to the H_3O^+ as well as the protons "lost" according to $H_2O \rightarrow OH^- + H^+$ is extremely small at first but grows exponentially. The upper "fill level" indicates the basic value of the proton potential in an acid–base system H_3O^+/H_2O, and the lower one shows the corresponding basic value in the H_2O/OH^- system.

In biological systems, the proton potential μ_p is often adjusted to certain values: in human blood it is fairly close to (-42.2 ± 0.3) kG, in stomach acid at around -10 kG, in urine at about -30 kG, and in the small intestine at about -50 kG. There must be buffer systems present that compensate for the water's lack of buffer capacity. Graphically speaking, the two "containers" in Figs. 7.8b and 7.9 are

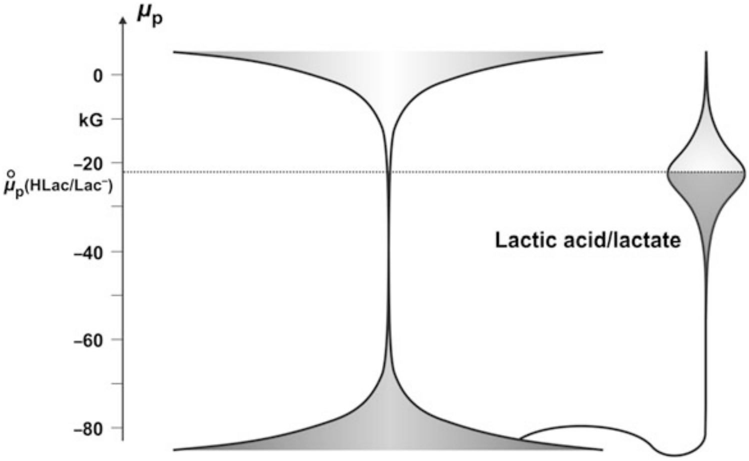


Fig. 7.10 Potential diagram for protons in the buffer system lactic acid/lactate in an aqueous solution (100 mL, 1 kmol m^{-3}, 298 K).

connected (Fig. 7.10). Expressed mathematically, this means that the buffer capacities of several acid–base pairs in a solution are added up:

$$B_{\text{p,total}} = B_{\text{p}}(\text{Ad/Bs}) + B_{\text{p}}(\text{Ad*/Bs*}) + \ldots .$$

The lack of buffer capacity in water can be compensated for by adding a suitable buffer system of an approximately equimolar mixture of the acid and its corresponding base because B_p as well as b_p will then be greatest. Figure 7.10 illustrates the relation using the example of the pair lactic acid (CH_3–CHOH–COOH, abbreviated HLac)/lactate (Lac). As already discussed, the "proton reservoir" produced by such pairs has the greatest capacity when it is half full. This occurs in this case in the range of proton potential where the buffer capacity of the water is extremely small.

When there is enough excess quantity of lactate Lac^- present together with its protonated form HLac (lactic acid) compared to the other dissolved pairs Ad/Bs, Ad*/Bs*, ..., this *buffer system* determines the value of the proton potential. The bases are protonated or the acids deprotonated until the same proton potential is present everywhere. This is essentially determined by the level equation (7.12) of the buffer system lactic acid/lactate. When the lactate is half protonated, i.e., if $c(\text{Lac}^-) = c(\text{HLac})$, then we have:

$$\mu_{\text{p}} = \overset{\circ}{\mu}_{\text{p}}(\text{HLAc/Lac}^-) = -22 \text{ kG}.$$

This is why it is possible to buffer a solution at a given proton potential by choosing an acid–base pair whose basic value lies somewhere around the desired proton potential. In biology, the most important buffer is the carbon dioxide/hydrogen carbonate system with a basic value of −36.4 kG: $CO_2|g + H_2O|l \rightleftarrows HCO_3^-|w + H^+|w$. It is by far the most important part of the buffer system in the blood which maintains the proton potential of blood rather precisely between −42.5 and −41.9 kG (at 37 °C) and balances deviations caused by metabolism. A constant proton potential is indispensable to life because values greater than −38 kG or less than −46 kG often result in death.

As a result of the assumed excess and the consequent large buffer capacity, proton gain or loss leads to only slight μ_p shifts in the buffer system. For clarity, we will look more closely at the example of the lactic acid/lactate system. A buffer solution that contains lactate as well as lactic acid at a concentration of 0.1 kmol m^{-3} shows a proton potential μ_p of −22 kG. If 1 cm^3 of hydrochloric acid at a concentration of 1 kmol m^{-3} is added to one liter of this solution, it adjusts to a new proton potential μ_p'. Adding 0.001 mol HCl to the original 0.1 mol lactate in 1 L reduces the lactate by about 0.001 mol according to $Lac^- + H^+ \rightarrow HLac$, while the lactic acid increases by that much. Applying the level equation results in a new proton potential μ_p':

$$\mu_p' = \overset{\circ}{\mu}_p(\mathrm{HLac}/\mathrm{Lac}^-) + RT\ln\frac{c(\mathrm{HLac})'}{c(\mathrm{Lac}^-)'}, \text{meaning}$$

$$\mu_p' = -22 \times 10^3\,\mathrm{G} + 8.314\ \mathrm{GK}^{-1} \times 298\ \mathrm{K} \times \ln\frac{0.1 - 0.001}{0.1 + 0.001} = -21.95\ \mathrm{kG}.$$

Adding the acid has only changed the proton potential by 0.05 kG.

If, however, the same amount of 1 cm^3 of hydrochloric acid is added to pure water, the proton potential μ_p'' will be

$$\mu_p'' = \overset{\circ}{\mu}_p(\mathrm{H_3O^+}/\mathrm{H_2O}) + RT\ln c_r(\mathrm{H_3O^+})$$

[according to Eq. (7.3)] and therefore

$$\mu_p'' = 0\ \mathrm{G} + 8.314\ \mathrm{GK}^{-1} \times 298\ \mathrm{K} \times \ln 0.001 = -17\ \mathrm{kG}.$$

By adding the acid, the proton potential has shifted by 23 kG in relation to that of pure water with −40 kG (compared to a change of only 0.05 kG ! in the case of the buffer solution).

Having introduced the concept of buffers, and having made it graphically clear in potential diagrams, we can now understand why the proton potential changes only very slowly until shortly before the equivalence point when the base of a weak alkaline pair (such as ammonia solution) is titrated with the acid of a strong acidic pair (Fig. 7.11). If the “communicating containers” are slowly filled with protons during titration, the level and the proton potential along with it will, at first, be largely determined by the “wide-bellied” proton reservoir of the buffer system

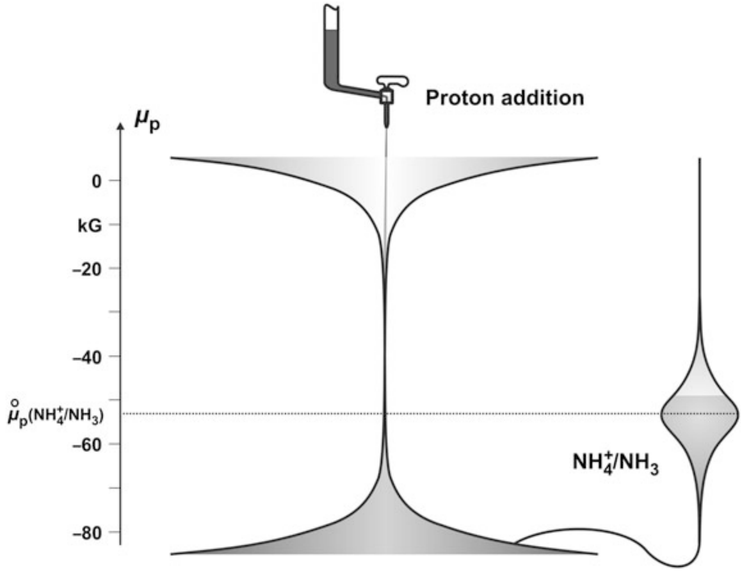


Fig. 7.11 Illustration of titration, using a potential diagram, of the base of a weak alkaline pair with the acid of a strong acidic pair.

NH_4^+/NH_3. Greater amounts of protons can be added especially in the range that is most “rounded out” without the level changing noticeably. However, if the proton reservoir is completely full (equivalence point), a drastic change of proton potential occurs when more protons are added. However, this change slows down in the “funnel area” of the “exponential horn.”

7.7 Acid–Base Indicators

Acid–base pairs with strongly contrasting colors are also interesting. Normally, these are large, water-soluble organic molecules. In tiny amounts, they are used as *indicators*. By themselves and in equal amounts in a solution, the members of these pairs produce a certain color mixture and a certain proton potential $\overset{\circ}{\mu}_p(\text{HInd}/\text{Ind}^-)$, which is characteristic of the indicator system because indicator acids (HInd) and bases (Ind^-) obey the level equation (7.12) as well:

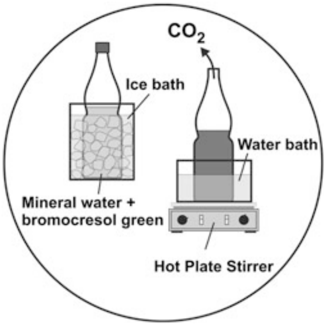
$$\mu_p = \overset{\circ}{\mu}_p(\text{HInd}/\text{Ind}^-) + RT\ln\frac{c(\text{HInd})}{c(\text{Ind}^-)}. \tag{7.21}$$

When the proton potential in a solution is raised by adding an excess quantity of the acid of a stronger acidic pair, for example, the indicator base disappears due to

Table 7.3 Standard values of some acid–base indicators and the corresponding changes of color (acid color—base color).

Indicator	$\mu_p^{\ominus}$ (kG)	Color change
Thymol blue	−10	Red—yellow
Bromophenol blue	−22	Yellow—blue
Bromocresol green	−28	Yellow—blue
Methyl red	−29	Red—yellow
Bromothymol blue	−41	Yellow—blue
Phenol red	−45	Yellow—red
Thymol blue	−51	Yellow—blue
Phenolphthalein	−54	Colorless—pink
Alizarin yellow	−64	Yellow—red

Experiment 7.3 *Acidity effect of mineral water*: If the indicator bromocresol green is put into a bottle of very cold mineral water, the solution turns yellow. When the bottle is opened at room temperature or the content heated, a large portion of the carbon dioxide escapes and the indicator color changes to green and finally to an intense blue.



protonation, leaving only the color of the indicator acid visible. Just the opposite occurs when the proton potential is lowered. In this case, the acid is eliminated and the pure color of the base appears. Therefore, the color indicates whether μ_p is greater, smaller, or equal to $\overset{\circ}{\mu}_p$ (HInd/Ind$^-$). Table 7.3 shows the standard values of some acid–base indicators.

An interesting example for the change of an indicator in color due to a change of proton potential is the experiment about the acidity effect of sparkling water (Experiment 7.3). The reason for this acidity effect is the hydrogen carbonate that is produced when carbon dioxide dissolves in water. When it is cold and under pressure, it provides enough protons p which form oxonium ions with water:

$$CO_2|g + H_2O|l \rightleftarrows CO_2|w,$$
$$CO_2|w + 2\ H_2O|l \rightleftarrows H_3O^+|w + HCO_3^-|w.$$

The indicator's change of color can also be used to indicate the end point of acid–base titrations. This is possible because the proton potential climbs strongly while

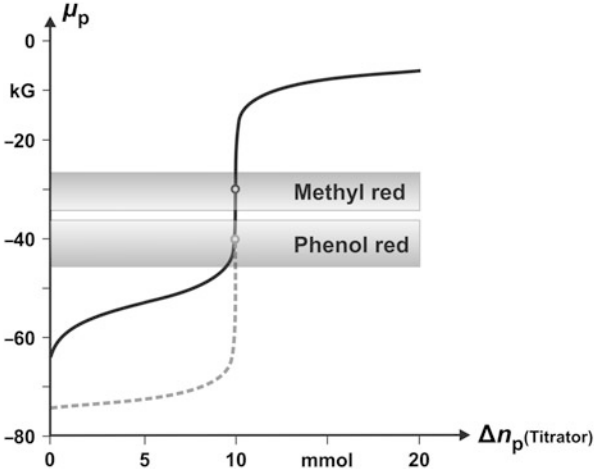


Fig. 7.12 Titration curves of weak alkaline pair–strong acidic pair (*black solid line*) and strong alkaline pair–strong acidic pair (*gray dotted line*) as well as the transition intervals of two indicators.

an acid of a strong acidic pair is being added, as we have seen in a previous section. This happens exactly when the base, whose concentration is not known, has been used up. Therefore, the indicator must be chosen so that its characteristic proton potential $\overset{\circ}{\mu}_p(\text{Hind}/\text{Ind}^-)$ lies between that of the acid–base pairs in the unknown solution and in the standard solution. This should correspond as well as possible to the proton potential at the equivalence point. For this reason, the indicator methyl red is suitable for the titration of the base of a weak alkaline pair with the acid of a strong acidic pair, but the indicator phenol red is not (Fig. 7.12). The latter can, however, be used in the titration of the base of a strong alkaline pair with the acid of a strong acidic pair. In this case, the changes of potential are so drastic that even with indicators of more strongly deviating $\overset{\circ}{\mu}_p$ values such as phenolphthalein, precise results can be obtained.

Indicators are, themselves, acids (HInd) or bases (Ind^-) so they also use up the standard solution when turning their color. They are employed in very small concentrations in order to keep possible errors to a minimum.