Chapter 3
Liquid Junction Potentials

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3.1 Introduction

The liquid junction potential (LJP), as considered in relation to practical aspects of reference electrodes, is a rather bothering experimental problem. The additional and always unknown potential drop between the electrolytes of the electrode under study and of the reference electrode is harmful for the accuracy of potential measurements. In addition, the existence of this drop disturbs the equilibrium in the circuit (if any) and complicates stabilization of nonequilibrium systems.

Simultaneously, the LJP is an exciting phenomenon for the theory of electrochemical systems. Its modeling combines various types of theory and provides the results widely accepted in practice. Another remarkable aspect is the existence of LJPs in a wide variety of systems with essentially different viscosity, permittivity, and molecular structure. This is always advantageous for theory verification.

The LJP has a meaning of Galvani potential, i.e., *its exact value cannot be measured by definition* [1]. This results in the need of various approximations from both experimental and modeling sides. Generally, both the solvent and the electrolyte can be different in two contacting liquid phases (1) and (2), and it is assumed [2] that the quantity of the LJP can be presented by two additive contributions induced by heterogeneous distribution of ions and polar molecules, respectively:

$$\Delta\phi_{\mathrm{LJ}} = \Delta\phi_{\mathrm{ion}} + \Delta\phi_{\mathrm{solv}}. \tag{3.1}$$

The ionic contribution is given by the equation:

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$$\Delta\phi_{\text{ion}} = -\frac{RT}{F}\int\limits_{(1)}^{(2)}\sum\frac{t_i}{z_i}\,\mathrm{d}\ln a_i - \frac{RT}{F}\int\limits_{(1)}^{(2)}\sum\frac{t_i}{z_i}\,\mathrm{d}\mu_i^{\ominus}, \tag{3.2}$$

where t_i is the transport number of the i-th ion, that is, the portion of current transferred by this ion through the solution, a_i is the individual activity of the i-th ion (*immeasurable quantity!*), and $\mu_i^{\ominus}$ is the standard chemical potential of the i-th ion. For scientists mostly working in a single solvent (e.g., with aqueous potentiometric techniques), the definition of the LJP is typically limited to the first right-hand term in Eq. (3.2), and they associate the LJP with the so-named diffusion potential: $\Delta\phi_{\text{LJ}} = \Delta\phi_{\text{diff}}$.

The term "diffusion potential" results from the fact that the space separation of charge is initially induced by diffusion. In contrast, for people dealing with solvent effects (e.g., in organic electrochemistry), the solvent contribution attracts more attention, including solvent effect on $\mu_i^{\ominus}$. The principle (mostly psychological) difference results from strongly different experimental and model approaches applied under these two circumstances. Strictly speaking, even in the absence of electrolyte, the diffusion layer exists at the boundary of two miscible liquids [2–4]. However, usually an inhomogeneous distribution of molecules (dipoles) results in a lower potential drop than the drop resulting from the redistribution of ions.

The classification of LJP effect considered below, mainly takes into account the nature of the potential drop at various types of liquid–liquid boundaries. One should realize that the problem of quantitative modeling and/or precise experimental separation of various contributions to the LJP of mixed nature still remain a challenge, when the limiting cases (predominating contribution of one type) already found more or less reasonable solutions.

This chapter is arranged as follows: Sect. 3.2 presents brief comments to the LJP between two different molecular solvents; Sect. 3.3 is devoted to the most advanced area, the LJP between two different electrolyte solutions in a certain solvent (known also as diffusion potential) and includes some comments concerning the temperature-induced LJP in these systems; Sect. 3.4 contains brief notes about LJPs in solvent-free systems, namely melts and room temperature ionic liquids (RTILs); the concluding Sect. 3.5 presents various specific cases of LJPs and outlines the links with electroanalysis, especially ion-selective electrodes, the functional properties of which are strongly affected by diffusion potentials. This specific case should be considered separately because the membrane/solution interfaces (as well as the boundaries of immiscible liquids) keep the exact geometry of boundaries.

This chapter could not be written in the traditional encyclopedic style because the understanding of LJPs is still under development. In the new millennium, the boom of RTIL's introduced new ideas and systems into chemistry and physics of liquids. In parallel, computational modeling of liquid systems became more powerful. New experimental and computational results require joint fermentation under the supervision of theory, and this process will take some time. The goal of this chapter is to collect and to structure currently available facts and hypothesis and to warn the reader of simplified and straightforward considerations of LJPs.

3.2 The LJP Between Two Different Molecular Solvents

The most traditional approach to an experimental estimation of the LJP between two polar solvents consists in the measurement of the emf between two identical redox electrodes in these liquids. Basically this measurable quantity contains the difference of redox potentials in the solvents coexisting in the cell and $\Delta\phi_{\mathrm{LJ}}$ as described by Eqs. (3.1) and (3.2). The most usual goal of scientists is not to separate $\Delta\phi_{\mathrm{solv}}$ (and/or contributions to $\Delta\phi_{\mathrm{ion}}$), but to account for $\Delta\phi_{\mathrm{LJ}}$ as a whole when constructing universal potential scales for various solvents. However, a parallel analysis of the contributions to $\Delta\phi_{\mathrm{LJ}}$ is unavoidable in these studies; so fundamental information accumulates in the course of "more applied" research as a sort of by-product. One important note is necessary concerning the ionic contribution $\Delta\phi_{\mathrm{ion}}$ in experiments considered below: even if one and the same electrolyte is dissolved in two solvents forming a LJP, and concentrations in both solvents are equal, $\Delta\phi_{\mathrm{ion}}$ is in general nonzero [both right-hand terms in Eq. (3.2) are solvent dependent]. In general one even cannot consider this contribution as minor (it is only possible for chemically related solvents).

The requirements for a redox probe operating as a reference system in various solvents are listed in Sect. 1.2.5 (see also Chaps. 1, 2, and 6). The most popular is the *ferrocene/ferrocenium* (Fc^+/Fc) system proposed for the first time more than 50 years ago [5] and recommended by authoritative sources [6, 7]. The problem is typically considered for the case when temperature and pressure gradients are zero. The earlier (slightly naive) idea of this sort [8, 9] was to use Rb^+/Rb as an inorganic reference. The size of rubidium ions is certainly insufficient to provide low enough solvation energy, but this suggestion stimulated a number of detailed experimental studies of reference systems for nonaqueous electrochemistry (see e.g., [10, 11]) and by these means created a firm basis for the Fc^+/Fc research. Interesting historical remarks are given by Krishtalik [12–14].

The solvation energies of ferrocene and ferrocenium, being the crucial values, are often considered to be the sum of electrostatic, solvophobic (cavitational), and specific (dispersion/repulsion) components. In the framework of the usual simplified models, the cavitational specific contributions of Fc^+ and Fc species are thought to cancel out due to minor changes in size of the molecule upon reduction/oxidation and effective screening of the metal center by the cyclopentadienyl rings (this assumption agrees with recent quantum chemistry results [15]). The second assumption about small electrostatic contribution to the solvation energy of Fc^+, which can be neglected when transferring the system from one solvent into the other, seems more risky from a first glance. A simple analysis of the solvation of Fc^+ in terms of the Born model predicts the solvation energy difference of Fc^+/Fc in, to say, water and benzonitrile of ~10 kJ/mol, corresponding to a possible difference of standard potentials of ca. 0.1 V. Unfortunately computational results are still helpless: the variation of DFT functional and basis sets induces an uncertainty comparable with 0.1 V for Fc^+/Fc couple [16]. When dealing with solvation energy differences rather than absolute values, the discrepancies are undoubtedly smaller, but the accuracy of these calculations still remains questionable [17, 18].

The comparison becomes more solid when the data for Fc^+/Fc and relative redox pairs in different solvents are considered in parallel [e.g., for *bis*(*biphenyl*)*chromium* (1/0) (BCr^+/BCr) or for *cobaltocenium*/*cobaltocene* (Cc^+/Cc)]. A relative redox probe containing the anion (carborane compound, bis-*o*-dicarbollyl-nickel) was studied for comparison [12]. A consideration of the potential differences in various solvents, rather than relative redox potential values, eliminates the LJP. The tabulated values for differences between the formal potentials of BCr^+/BCr and Fc^+/Fc couples in 22 solvents with significantly different static permittivity values are equal within the accuracy of few mV [7]. Similarly, the differences of the formal potentials of Fc^+/Fc and Cc^+/Cc in five aprotic solvents and three aqueous–organic mixtures remain practically constant within the limits of experimental error [12], when the difference in water is somewhat larger, ca 40 mV. The comparison with aqueous systems is slightly risky, as the reactants under study are not so stable in water.

The cobaltocenium system is of special interest, as in some solvents the second (reductive) process can be observed for Cc, and one can extract the experimental difference of two redox potentials dealing with only one model reactant. The redox potentials of the $Cc^+/Cc/Cc$ couples were reported for usual aprotic solvents [12] and some specific low-dielectric solvents (namely monoglyme, dichloromethane, and diglyme) [19], as well as for water mixtures with these solvents [19, 20]. Corresponding water−solvent LJP values were evaluated on the basis of these data, mostly finding themselves in the range of 0.2–0.3 V. In general LJPs do not correlate with the solvent dielectric constant, but they are possibly affected by the hydrophylic or hydrophobic nature of the solvent. This result indicates indirectly the pronounced contribution of $\Delta\phi_{\mathrm{solv}}$.

To separate approximately this contribution to $\Delta\phi_{\mathrm{LJ}}$ [Eq. (3.1)], the studies of (mixed solvent)/(pure solvent) junctions [3] are rather informative. Under more or less ideal conditions (no hydrogen bonds, etc.), the dipole–dipole interactions at the boundary are expected to result in a linear dependence of $\Delta\phi_{\mathrm{solv}}$ on the molar composition of the mixed solvent. Correspondingly, the same trend is expected for measurable emf's of the model cells with the above-mentioned junction, and it was really observed for usual aprotic solvents with not too low polarity. The qualitative models of smooth and stepped dipoles distribution in the diffusion layer [3, 4] were suggested in relation to these experiments (see also discussion in review [2]). These models can be further improved if the molecular structure of the solvents is involved. The topic is surely "under construction," as well as more bulky mixed solvent research.

Despite the history of LJPs at solvent/solvent interface is rather old, the area is still opened for scientific novelty. This results from the endless diversity of mixed solvents and less predictable trends in applied electrochemistry. Namely, new challenges arise from the development of lithium batteries [21], and it is natural to assume that future trends in electrochemical energy conversion will be also "nonaqueous" because of the crucial role of wide potential windows. It is difficult to predict whether molecular or ionic liquids will dominate in these future applications, but the background for LJP phenomena in both media goes from the basic knowledge of LJP for molecular solvents.

For solvents (1) and (2) with a common binary electrolyte, the LJP can be presented by combination of chemical potentials of ions (or, in other words, by the energies of ions transfer):

$$\Delta\phi_{\mathrm{LJ}} = \left[\mu^{(1)}_{\mathrm{cation}} - \mu^{(2)}_{\mathrm{cation}} - \mu^{(1)}_{\mathrm{anion}} + \mu^{(2)}_{\mathrm{anion}}\right]/2. \tag{3.3}$$

This equation certainly contains the unknown values related to individual ions. However, it is sometimes useful for the estimation of the LJP from the data on the energy transfer of salts (of course with inclusion of some extrathermodynamic assumptions concerning the energies of single ions transfer).

The energy of ions transfer can be estimated from potentiometric data for the interfaces of two immiscible electrolyte solutions (ITIES) [22]. Early data for water/octane are tabulated in ref. [8]. However, "oil-type" solvents forming ITIES are not so common in usual nonaqueous electrochemistry. The specific details of the estimation of LJPs for completely and partly miscible organic liquids can be found in ref. [23].

3.3 The LJP at Solution/Solution Interface

Really inspiring fragments of the history of science are concerned with the quantitative theory of the LJP and its experimental verification just for the case when the nature of solvent is the same for both solutions (1) and (2) having equal temperatures and pressures. Another general assumption is the absence of convection (however, slow time-independent convection is not crucial for model estimates). The goal of this section is to present briefly the links between basic LJP knowledge and modern practice of LJP arrangement.

3.3.1 The LJP at Solution/Solution Interface (One and the Same Solvent)

A LJP resulting exclusively from concentration gradients of ions is most frequently called a diffusion potential drop $\Delta\phi_{\mathrm{diff}}$. If the solvent from both sides of junction is the same, $\mu_i^{\ominus}$ is constant along the boundary, and Eq. (3.2) is reduced to

$$\Delta\phi_{\mathrm{LJ}} = \Delta\phi_{\mathrm{diff}} = -\frac{RT}{F}\int_{(1)}^{(2)} \sum \frac{t_i}{z_i}\,\mathrm{d}\ln a_i. \tag{3.4}$$

In the first approximation, $\Delta\phi_{\mathrm{diff}}$ can be estimated by substituting corresponding concentrations c_i for the partial activities a_i. The resulting value looses the meaning of Galvani potential, but despite the left-hand quantity still cannot be measured, the right-hand term can be calculated by adopting a model approach to the concentration distribution of ions in the boundary region. The basis for this calculation is the electroneutrality approximation discussed in ref. [24] in a popular form with impressive historic notes.

There are two types of $\Delta\phi_{\mathrm{diff}}$-related model problems, dynamic and steady state, both being of high practical interest. Informative brief reviews of dynamic solutions for various types of electrolyte combinations in the junctions are available in refs. [5, 25] in addition to original simulation results. Principle explanations concerning model assumptions and limitations can be found in ref. [26]. The dynamic problem consists in the simulation of charge separation transients and/or spatial distribution of ions concentrations. At the starting point (zero time) the diffusion gradients between solutions (1) and (2) for all ions are determined by the bulk concentrations, which are the principle parameters being experimentally controllable. Typically the mobilities of ions are also available parameters depending on the electrolyte nature and concentration, solvent nature (mostly viscosity), pressure, and temperature. When the diffusion of ions starts, and the mobilities of the ions of at least two types are different (which is typical), a spatial charge separation appears immediately. This prompts a migration component, which facilitates the transport of the "slower" ions, and hinders the movement of the "faster" ions. After some period (up to a μs for usual molecular solvents at room temperature) the interplay of the opposite diffusion and migration flows results in a steady state. Under these stationary conditions, the total fluxes of anions and cations of one and the same electrolyte are equal and no further charge separation takes place. Correspondingly, electrolytes continue to move as a single whole with time-independent rate.

It should be stressed that this stationary situation is still a nonequilibrium one. The quantitative result depends on parameters mentioned above and on the geometry of the boundary region. The latter, in its turn, depends on the degree of spreading of the initial sharp boundary during the period until the steady state is established. Typically, the steady-state $\Delta\phi_{\mathrm{diff}}$ values are calculated in the framework of the models of Planck [26, 27] and Henderson [26, 28, 29], as the most conventional.

In Planck's model for a sharp boundary, for 1,1-electrolyte,

$$\Delta\phi_{\mathrm{diff}} = \frac{RT}{F}\ln\xi, \tag{3.5}$$

where function ξ can be found from a transcendent equation in which "+" and "−" denote the sets, which consist of all cations and of all anions, respectively, and λ denotes the limiting conductivity of the corresponding ion:

$$\frac{\xi\sum_{+}\lambda_{+}^{(2)}c_{+}^{(2)}-\sum_{+}\lambda_{+}^{(1)}c_{+}^{(1)}}{\sum_{-}\lambda_{-}^{(2)}c_{-}^{(2)}-\xi\sum_{-}\lambda_{-}^{(1)}c_{-}^{(1)}}=\frac{\ln\left(\frac{\sum_i c_i^{(2)}}{\sum_i c_i^{(1)}}\right)-\ln\xi}{\ln\left(\frac{\sum_i c_i^{(2)}}{\sum_i c_i^{(1)}}\right)+\ln\xi}\cdot\frac{\xi\sum_i c_i^{(2)}-\sum_i c_i^{(1)}}{\sum_i c_i^{(2)}-\xi\sum_i c_i^{(1)}}. \tag{3.6}$$

Henderson equation, which has gained wider acceptance, corresponds to the so-called free diffusion boundary, i.e., to a degraded diffusion layer with approximately linear concentration distribution along the normal to the boundary. The traditional form of Henderson equation (for concentrations c having the units of normality) is as follows:

$$\Delta\phi_{\mathrm{diff}}=\frac{RT}{F}\cdot\frac{\sum_i\left(\frac{\lambda_i}{z_i}\right)\cdot\left(c_i^{(2)}-c_i^{(1)}\right)}{\sum_i\lambda_i\cdot\left(c_i^{(2)}-c_i^{(1)}\right)}\ln\frac{\sum_i\lambda_i c_i^{(1)}}{\sum_i\lambda_i c_i^{(2)}}. \tag{3.7}$$

The equation was derived for the case of a smeared-out boundary and linear spatial distributions of concentrations.

Two particular types of simplified systems attracted special attention. The first is the liquid junction between solutions of one and the same electrolyte with different concentrations (sometimes called liquid junctions of Lingane's type 1 [30]). For such a junction formed by 1,1-electrolyte solutions, both Eqs. (3.6) and (3.7) are reduced to the formula

$$\Delta\phi_{\mathrm{diff}}=\frac{RT}{F}\cdot\frac{\lambda_{-}-\lambda_{+}}{\lambda_{-}+\lambda_{+}}\ln\frac{c^{(1)}}{c^{(2)}}, \tag{3.8}$$

where c without subscript stands for concentrations of solutions. The actively studied junctions of another type (liquid junctions of Lingane's type 2 [30]) are formed by different electrolytes of equal concentrations. In this case

$$\Delta\phi_{\mathrm{diff}}=\frac{RT}{F}\cdot\ln\frac{\Lambda^{(1)}}{\Lambda^{(2)}}. \tag{3.9}$$

Equation (3.9) is also known as the Lewis–Sargent formula [31]. This formula operates with equivalent conductivities of solutions Λ, not of the ions. The paper [31] published 1 year after Henderson's papers played a historical role. The cells of the same geometry as were used in [31] are still utilized for emf measurements. These cells with free diffusion boundary are sometimes called Lewis–Sargent cells. Another important note in ref. [31] concerns the search of conductivity values.

In contrast to Planck's initial idea, it was suggested to use concentration-dependent conductivities instead of the limiting values.[1]

To judge what boundary is "sharp" (Planck's model) or smoothed (Henderson's model), one should consider the thickness of the real diffusion layer under steady-state conditions. Typically it is of the order of μm, i.e., much larger than the ionic size, if the shape of the boundary is not regulated by some mechanical means. The specific size effect appears if the boundary is formed in microchannel configuration and when the diffusion length is comparable with the total distance between the channel walls. The problem is considered quantitatively in refs. [32, 33], in relation to devices for microanalysis.

Generally, Eqs. (3.5)–(3.7) yield very similar results; however, for junctions with a pronounced difference in ion mobilities (like HCl⁝LiCl), the difference of the two model predictions can reach up to 10 mV. A specific feature of the Planck equation is the existence of two mathematical solutions, the first being close to that of Henderson, and the second one being independent of the solution concentration and of no physical meaning [34].

It is useful to mention a number of early experimental studies aimed at estimation of LJPs and verification of Eqs. (3.5)–(3.7). These studies are still of interest as a source of precise tabulated data with the accuracy achieving at least 0.1 mV, and they contain a lot of experimental details sometimes missed in modern measurements despite the seemingly higher technical level of electronic voltmeters. The earliest stage of this research, when the data on ionic mobilities were rather limited, can be imagined from the papers of Gumming [35, 36]. From the later (most active) period of 1910–1930s, the conclusive or most detailed papers of each series are mentioned here. Very important series in relation to both LJPs and single ion activities (these problems cannot be separated) were published by MacInnes (see, e.g., [37–39]) and Harned (see, e.g., [40, 41]; note that the most popular cell for pH measurements is still the Harned cell [42]). These data were collected for a wide range of concentrations, conductivities, and transfer numbers, and by these means formed the basis to verify theoretical relationships. Experiments with sucrose solutions instead of water [43] should be also mentioned, as important for involvement of even more wider range of conductivities. Critical reviews of earlier works, in combination with original data, were published by Guggenheim [44, 45].

The determination of activity coefficients of individual ions is still a widely discussed application of LJP models. From thermodynamic point of view it is impossible, so the problems of diffusion potential calculation and single ion activities determination form a sort of vicious circle. To calculate the former

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[1] The problem looks slightly philosophic, as any calculated $\Delta\phi_{\mathrm{diff}}$ values cannot pretend on exact agreement with experiment because of model approximations. In [31] the values computed on the basis of concentration-dependent conductivity for 0.1–0.2 M solutions demonstrated better agreement with experimental emf data as compared to the values based on the limiting conductivity, but both experimental and theoretical values have no exact meaning of LJP. In practice, when calculations are required for junctions with high solution concentration, there are simply no quantitative data on conductivity.

value, one should know the latter values. These values, in their term, can be only determined if the diffusion potential is completely eliminated (which is impossible in general), or its values for the both sides of salt bridge are known. This finally means that the former values can be calculated by some other ways, which means some model approximations, etc. State of the art can be understood from the brief reviews "Single-Ion Activity: Experiment versus Theory" [46], "The Impossibility of Measuring Individual Ion Activity Coefficients Using Ion-Selective Electrodes," [47] and "The nature of single-ion activity coefficients calculated from potentiometric measurements on cells with liquid junctions" [48], and the follow-up discussion [49]. About recurrent attempts of a mathematical factorizing concentration functions to access individual activity coefficients of ions see refs. [50–52].

Another area in near relation to diffusion potential and individual ions activity is the physical chemistry of ion selective electrodes.

3.3.2 Elimination of Diffusion Potential (Principal Aspects)

In practice, in place of model LJP calculations and corresponding emf corrections, the elimination of the diffusion potential is conventionally applied. This is achieved by introducing the so-called "salt bridges" filled with concentrated solutions of salts, which satisfy the condition $t_+/z_+ = t_-/z_-$ (see Chap. 4). For a symmetric electrolyte, this simply means that anions and cations have very close diffusion coefficients, and transport numbers of both ions are ~0.5. When the salt bridge is located between the solutions of the working and reference electrodes, two LJPs appear instead of the initial single LJP (which is attempted to be eliminated). Both new LJPs are nonzero and can be rather high. However, under the above-mentioned condition these two potential drops are of close absolute value and of the opposite sign, compensating each other to some extent. One can easily obtain this result, e.g., from Eq. (3.7).

A widely known example is a saturated KCl solution (which concentration achieves 4.8 mol/kg at 25 °C, $t_+ = 0.48$, $t_- = 0.52$). In aqueous solutions, potassium and ammonium nitrates are also suitable, as well as some rubidium and cesium salts. Expensive but impressive versions are CsCl (11.3 mol/kg at 25 °C, $t_+ = 0.5025$, $t_- = 0.4975$) and RbCl (7 mol/kg at 25 °C, $t_+ = 0.5009$, $t_- = 0.4991$) [53]. The requirement of equal transport numbers is less important as compared with that of high concentration of electrolyte solution, which fills the bridge [54–56]. There is also an interesting example of an unsymmetrical electrolyte, lithium sulfate, which satisfies the requirement mentioned above because the lithium cation has a transfer number ca. twice lower than the sulfate anion [57]. Lithium sulfate bridges are of interest for organic and water–organic media with low KCl solubility. A suitable version of the salt bridge can be chosen for any type of cells, when taking into account the purposes of research or application [56].

Recently, salt bridges containing water-stable and moderately hydrophobic RTIL's with substituted phosphonium cation and fluorinated sulfonyl amide anion [58–60] were demonstrated to be advantageous, as well as mixtures with more hydrophobic RTIL [61]. The cell stability provides a satisfactory accuracy for the determination of pH and individual activity coefficients of small ions. The prospects of RTIL salt bridges are considered below in Sect. 4.2. Here, we should mention that this useful invention can stimulate the development of theory for solution|RTIL boundaries and interfaces. To extend the traditional approaches mentioned in Sect. 3.3.1, one should consider the transport of large RTIL ions first in RTIL and later in water, which is not so trivial and requires additional parameters. This theoretical problem is important for practice as well, at least in relation to the stabilization time of the bridge. Currently available data [58, 61] demonstrate that stabilization of potential drops at water|RTIL boundary requires up to 10^3 s, which exceeds the values for solution|solution interfaces by many orders of magnitude and can be hardly explained by the difference in viscosities. The initial idea of the authors [62] was to escape this problem by using quasi-Nernstian boundaries.

Special difficulties arise when suspensions of solid particles (e.g., soil) are studied instead of solutions. For suspensions, the diffusion potential appears to be anomalously high as compared to the parent solutions because the diffuse layers of suspended particles contribute to the apparent quantity. The technique of LJP elimination for suspensions assumes the comparative measurements in the cells of various configurations [63].

3.3.3 LJP Optimization by Means of Cell and Salt Bridge Construction

The early studies of aqueous LJPs were concentrated on experimental verification of Planck and Henderson models. As the difference of these models was related in particular to the geometry of the diffusion layer, some efforts were made to study various cell/salt bridge geometries. To ensure steady state LJPs, the "free diffusion" configuration was compared with a cell possessing a "continuous mixture layer" [44]. Early experiments with flowing junction [45, 64] resulted in a very stable cell operation (see also about stopping of the flow effect in ref. [65]). The general approach was always a comparison of data of cells with and without transference, the control experiments in symmetric cells, and in the cells with various types of salt bridges. Despite classical early studies were never reduced to determination of LJP by simple subtraction of the data for various cells, the simplified procedure of this sort is frequently applied for the rough estimate of LJP contributions.

These estimates are really useful for stability tests when new constructions of salt bridges are considered. A respective review is available now [66] (see also Chap. 4). A special comment is required concerning the mutual location of a Luggin capillary salt bridge and the main compartment of the electrochemical cell when a penetration of KCl (or another LJP eliminating electrolyte) is undesirable. In this

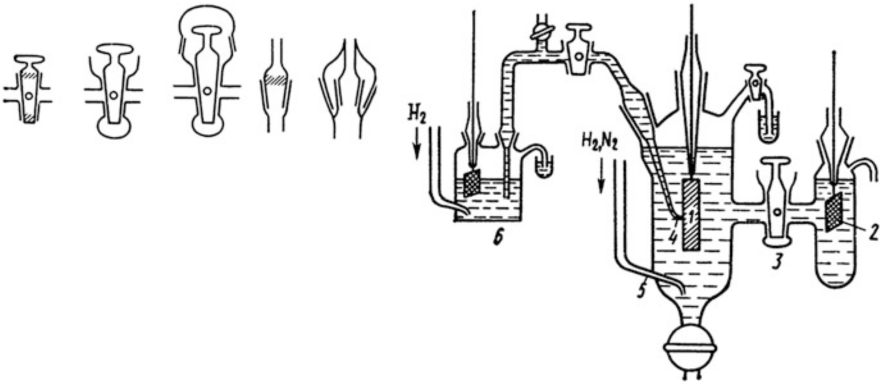

Fig. 3.1 Various types of glass junctions for electrochemical cells (*left*) and an example of the cell with separated compartments (*right 1*: working electrode, *2*: counter electrode, *3*: stopcock junction, *4*: Luggin capillary, *5*: gas inlet, *6*: hydrogen reference electrode) [71]

case it is always advantageous to locate the bridge below the main compartment of the cell, not above, because gravitationally induced convection provides an essential contribution to electrolyte transfer.

Various permeable membranes were applied to decrease the rate of electrolyte diffusion under steady state [67], in particular a collodion membrane first proposed in ref. [68] became rather popular. In contrast to ion-selective membranes, no Donnan potential is established when collodion membrane is used. These membranes are introduced to stabilize the system for long-term operation, not to affect LJP as is. Many inert viscous substances and porous inert ceramics can serve for the same purpose, and this approach is widely used in modern technologies of miniaturized reference electrodes for applications. Various types of diaphragms (including polymer and ceramics) are used in industrial pH measurements as well [69].

For basic interfacial electrochemistry, it is always better to use cells with reliably separated compartments. For glass cells, the best is to use thoroughly finished glass stopcocks. In this case the thickness of liquid layer is of the order of μm, and electrolyte diffusion from the salt bridge is rather slow. For long experiments and/or solutions with highly mobile hydronium ions, the bridges with two consecutive stopcocks can be recommended, like applied for the measurements in deuterated aqueous solutions with the use of protium-based hydrogen [70]. A classical design of these cells for precise electrochemical measurements is presented in ref. [71] (despite this book is published in Russian, the pictures themselves can be informative for any audience, see, e.g., in Figure 3.1).

The most illustrative examples of LJP minimization and optimization can be found in the traditional area of pH measurements [42, 72]. It forms an important part of Bates–Guggenheim convention [21]. However, one should note that this convention also assumes an extrathermodynamic assumption, in which unknown accuracy is partly compensated by numerous calibrations. The example of later attempts to further improve LJP aspects of the glass electrode can be found in ref. [73].

Going to more technical applications, a simplified (and probably sufficient) approach to the estimation of LJPs is typical for channel devices in flow injection electroanalysis (see, e.g., [74]). The injection of solutions of different composition provides a serious risk of local compositional changes and by these means can affect the LJP. The goal of research in this area is mostly to minimize nonstationary LJP contributions. The measurements of pH in large-scale flows related to industrial applications are discussed in refs. [69, 75].

The problem of LJP correction of pH values for highly diluted solutions remains essential, and empiric corrections are still under discussion in practical analytical chemistry [76]. In relation to this problem, the study of "electrochemistry in pure water" [77] is of interest. In this case (no electrolyte added to high purity water) the LJP is unpredictably high and sensitive to occasional solution composition. The sometimes used Nafion membrane to separate the working electrode and a hydrogen reference electrode is certainly to be discouraged because of the introduction of an additional membrane potential.

3.3.4 Thermal LJP Between Solutions Having Different Temperatures

In early studies [78], the effect of temperature on LJP was considered exclusively in terms of Eq. (3.7). It was believed that the increase of T in RT/F multiplier is compensated partly or completely by temperature dependences of ionic mobilities. Much later Thermal LJP (TLJP) phenomenon was treated theoretically for balanced external pressure [79]. For the junction of two solutions of equal concentrations (the solvent and electrolyte has one common ion) with the temperatures T_1 and T_2 ($T_2 > T_1$), the equation for temperature-induced contribution contains new parameters the entropies of the transport of individual i-th ions (S_i):

$$\Delta\phi_{\mathrm{TLJ}} = -\frac{RT}{F}\int_{T_1}^{T_2}\sum\frac{t_i S_i}{z_i}\,\mathrm{d}T. \tag{3.10}$$

This TLJP is important for pH measurements at elevated temperatures. Key values of high temperature parameters for some usual 1,1-electrolytes are reported in ref. [79], and the equations for solid electrolyte-containing cells with temperature gradient are presented as well. Important note specially marked in later review [80] is related to the changes of the customary transport numbers with temperature (at elevated temperatures, NaCl is more suitable for LJP elimination than KCl). Quantitative information for both chlorides is available in ref. [81]. TLJP at solution/solution boundary is also of interest for applications related to corrosion. In this case the medium is technical water being rather diluted electrolyte, and not so low potential drops can arise (see example of TLJP research, e.g., in ref. [82]).

In melts, problem of TLJP (thermo-emf) always arises, and the emf correction is typically calculated from thermoelectric coefficients of phases in contact [83]. However, no detailed research of TLJP contribution to this correction is known. The problem is probably close to solvent/solvent junctions.

In [75], various advancements related to industrial pH control are considered as related to temperature effects on the uncertainty of the key quantity (automatically retractable probes, contactless connectors, "intelligent electrodes”). However, the author sadly concludes that recent developments have no or only a little improving effect.

3.4 LJP in Condensed Ionic Systems

The traditional treatment of LJP for melts is outlined in a classical monograph “Reference Electrodes Theory and Practice” [84]. For melt/melt junction containing three types of species ($i = 1$, 2, or 3), forming the salts “1–3” and “2–3” with equivalent conductivities Λ

$$\Delta\phi_{\text{diff}} = \frac{RT}{F}\cdot\left(\frac{\Lambda_{1-3}-\Lambda_{2-3}}{z_1\Lambda_{1-3}-z_2\Lambda_{2-3}}\right)\ln\frac{z_1\Lambda_{1-3}}{z_2\Lambda_{2-3}}. \tag{3.11}$$

Very approximate verification of this formula for RTILs can be arranged with the use of Ag-containing RTIL, which supports Ag^+/Ag reference [85]. For a single system with one common ion studied in ref. [85], Eq. (3.11) results in the value of ca. 80 mV, i.e., much higher than the values obtained earlier for high temperature melts. Comparison with experimental results is limited to assumptions related to model redox probes (Fc and Cc), as always.

Many questions still remain opened in fundamental research of RTILs, including LJP at the boundary of two ionic liquids and LJP at RTIL/molecular solvent boundary. The progress is expected from the studies of Fc^+/Fc and Cc^+/Cc reference scales by analogy with approach mentioned above in Sect. 3.2. It is already evident from comparison of formal potentials for Fc^+/Fc and similar decamethylferrocenium redox probe that the difference of solvation energy in various RTILs can result in potential shift up to 0.1 V [86]. Due to experimental difficulties related to high ohmic drops in RTIL, as well as to moisture and air sensitivity, the accuracy of potential measurements for redox couples is lower than compared to conventional interfacial electrochemistry [87–89], but it is enough to approach the same accuracy of LJP estimates. It is already evident that Born-like approaches are helpless for RTILs (even more than for molecular liquids).

To extend the traditional models of LJP to RTILs, one should solve the problem of possible changes of ion mobility after penetration into another medium.

The specific aspect for RTILs is the possibility of specific solvation of model redox reactant with either anion or cation. In the former case one cannot exclude that the traditional requirement for redox probe (point (ii) in Sect. 1.2.5, resulting from specific solvation of anions supported by hydrogen bonds) can be reconsidered, i.e., the redox couples containing neutral molecule as the oxidized (not reduced) form can be less sensitive to solvent nature.

In relation to LJP in condensed ionic systems, it is of interest to mention LJP in ionized gas formed by injection of salt solutions into high-temperature (1,800 K) flame located between two solution compartments with Pt reference electrodes [90]. Surprisingly, the dependence of potential difference on ions concentration in the flame and mobilities follows the trends for solution/solution LJP.

3.5 Membranes and Immiscible Liquids

These systems only rarely assume true equilibrium between solution and membrane. Typically they work under the mode of steady state nonequilibrium ions distribution, which means that stable diffusion potential is settled at membrane/ solution interface.

The examples of unified approach to diffusion potential modeling for solution/ solution (immiscible liquids) and solution/membrane boundaries can be found in refs. [25–27] and [91, 92]. There are already no doubts that diffusion potential contributes to the apparent membrane potential and affects strongly the calibration curves of ion-selective electrodes [26, 93, 94]. This can take place for glass electrode as well (see refs. related to pH measurements in Sect. 3.3.3).

The geometry of real polymer membranes still induces some problems with quantitative application of model calculations, and calibration procedure remains more or less empiric. However, the model systems imitating membranes, the interfaces of two immiscible electrolyte solutions (ITIES), are free from this shortcoming. Various types of LJP behavior for ITIES dependent on the ratios of ion partition coefficients are considered in ref. [95]; remarks in ref. [96] are also useful. The effect of initial concentration distribution on the temporal LJP behavior is considered in ref. [97] self-consistently for the limiting cases of thick membranes (assumed to operate as ion-selective electrodes) and thin membranes (assumed to imitate biological membranes).

General consideration of membrane potential and LJP in the context of experimental errors in potential measurements is available in a brief review [98]. The specific details for so-called "biological liquids" (like blood, urine, etc.) can be found in review [99].

References

1. Petrii OA, Tsirlina GA (2003) Electrode potentials. In: Bard AJ, Stratmann M, Gileadi E, Urbakh M (eds) Encyclopedia of electrochemistry, vol 1. Wiley-VCH, New York, pp 1–25
2. Izutsu K (2011) Anal Sci 27:685
3. Izutsu K (2008) Bull Chem Soc Jpn 81:703

4. Izutsu K (2010) Bull Chem Soc Jpn 83:39
5. Koepp HM, Wendt H, Strehlow H (1960) Z Elektrochem 64:483
6. Izutsu K (2002) Electrochemistry in nonaqueous solutions. Wiley-VCH, Darmstadt
7. Gritzner G, Kuta J (1984) Pure Appl Chem 56:461
8. Pleskov VA (1947) Uspekhi Khimii 16:254
9. Pleskov VA (1949) Zh Fiz Khimii 23:104
10. Kolthoff IM, Thomas FG (1965) J Phys Chem 69:3049
11. Parker AJ (1976) Electrochim Acta 21:671
12. Krishtalik LI, Alpatova NM, Ovsyannikova EV (1991) Electrochim Acta 36:435
13. Krishtalik LI (2008) Electrochim Acta 53:3722 [Erratum (2009) Electrochim Acta 54:4741]
14. Krishtalik LI (2008) Russ J Electrochem 44:43
15. Kuznetsov AnM, Maslii AN, Krishtalik LI (2009) Russ J Electrochem 45:87
16. Roy LE, Jakubikova E, Guthrie MG, Batista ER (2009) J Phys Chem A 113:6745
17. Namazian M, Lin CY, Coote ML (2010) J Chem Theory Comput 6:2721
18. Baik M-H, Friesner RA (2002) J Phys Chem A 106:7407
19. Bunakova LV, Khanova LA, Topolev VV, Krishtalik LI (2004) J New Mater Electrochem Syst 7:241
20. Khanova LA, Topolev VV, Krishtalik LI (2006) Chem Phys 326:33
21. Izutsu K (2011) J Solid State Electrochem 15:1719
22. Samec Z (2008) Interface of the immiscible liquids. In: Bard AJ, Inzelt G, Scholz F (eds) Electrochemical dictionary. Springer, Berlin, pp 359–360
23. Izutsu K, Kobayashi N (2005) J Electroanal Chem 574:197
24. Dickson EJF, Limon-Petersen JG, Compton RG (2011) J Solid State Electrochem 15:1335
25. Ward KR, Dickson EJF, Compton RG (2010) J Phys Chem B 114:4521
26. Sokalski T, Lingenfelter P, Lewenstam A (2003) J Phys Chem B 107:2443
27. Planck M (1890) Ann Physik 40:561
28. Henderson P (1907) Z Phys Chem 59:118
29. Henderson P (1908) Z Phys Chem 63:325
30. Lingane JJ (1958) Electroanalytical chemistry, 2nd edn. Prentice Hall, New York
31. Lewis GN, Sargent LW (1909) J Am Chem Soc 31:636
32. Kang KH, Kang IS (2004) J Electroanal Chem 566:331
33. Park J, Hun KY, Li X (2006) J Electroanal Chem 591:141
34. Damaskin BB, Tsirlina GA, Borzenko MI (1998) Russ J Electrochem 34:199
35. Gumming AC (1907) Trans Faraday Soc 2:213
36. Gumming AC (1912) Trans Faraday Soc 8:86
37. MacInnes DA (1915) J Am Chem Soc 37:2301
38. Noyes AA, MacInnes DA (1920) J Am Chem Soc 42:239
39. MacInnes DA, Yeh YL (1921) J Am Chem Soc 43:239
40. Harned HS (1916) J Am Chem Soc 38:1986
41. Harned HS (1926) J Phys Chem 30:433
42. Buck RP, Rondinini S, Covington AK, Baucke FGK, Brett CMA, Camxes MF, Milton MJT, Mussini T, Naumann R, Pratt KW, Spitzer P, Wilson GS (2002) Pure Appl Chem 74:2169
43. Scatchard G (1923) J Am Chem Soc 45:1716
44. Guggenheim EA (1930) J Am Chem Soc 52:1315
45. Guggenheim EA (1930) J Phys Chem 34:1758
46. Fraenkel D (2012) J Phys Chem B 116:3603
47. Zarubin DP (2011) J Chem Thermodyn 43:1135
48. Malatesta F (2000) J Solut Chem 29:771
49. Vera JH, Wilczek-Vera G (2012) J Chem Thermodyn 47:442 (continued in the same issue, pp 445, 449, 451)
50. Ferse A, Müller HO (2011) J Solid State Electrochem 10:2149
51. Malatesta F (2011) J Solid State Electrochem 10:2169
52. Ferse A (2011) J Solid State Electrochem 10:2173

53. Buizza C, Mussini PR, Mussini T, Rondinini S (1996) J Appl Electrochem 26:337
54. Chloupek JB, Danes VZ, Danesova BA (1933) Coll Czech Chem Commun 5:469
55. Chloupek JB, Danes VZ, Danesova BA (1933) Coll Czech Chem Commun 5:527
56. Sokalski T, Maj-Zurawska M, Hulanicki A, Lewenstam A (1999) Electroanalysis 11:632
57. Faverio CL, Mussini PR, Mussini T (1998) Anal Chem 70:2589
58. Sakaida H, Kakiuchi T (2011) J Phys Chem B 115:13222
59. Shimata M, Sakaida H, Kakiuchi T (2011) Anal Chem 83:164
60. Fujino Y, Kakiuchi T (2011) J Electroanal Chem 651:61
61. Zhang L, Miyazawa T, Kitazumi Y, Kakiuchi T (2012) Anal Chem 84:3461
62. Kakiuchi T, Tsujioka N, Kurita S, Iwami Y (2003) Electrochem Commun 5:159
63. Oman RF, Camxes MF, Powell KJ, Rajagopalan R, Spitzer P (2007) Pure Appl Chem 79:67, 81
64. MacInnes DA, Yeh YL (1921) J Am Chem Soc 43:2563
65. Scatchard G (1925) J Am Chem Soc 47:697
66. Kakiuchi T (2011) J Solid State Electrochem 15:1661
67. Lamb AB, Larson AT (1920) J Am Chem Soc 42:229
68. Fales HA, Stammelman MJ (1923) J Am Chem Soc 45:1271
69. Tauber G (2009) Technisches Messen 76:308
70. Rusanova MY, Tsirlina GA, Petrii OA (1993) Russ J Electrochem 29:412
71. Damaskin BB (ed) (1991) Praktikum po elektrokhimii (Lab works on electrochemistry). Vysshaya Shkola, Moscow, pp 5–23
72. Bates R, Popovych O (1981) Crit Rev Anal Chem 10:247
73. Brandariz I, Barriada JL, Taboada-Pan C, de Vicente MES (2001) Electroanalysis 13:1110
74. Adachi T, Suzuki H (2011) Sens Actuators B 156:228
75. Tauber G (2010) Technisches Messen 77:150
76. Kadis R, Leito I (2010) Anal Chim Acta 664:129
77. Huang H, Wang Q, Cha C-S, Lu J, Zhuang L (2011) Electroanalysis 23:577
78. Prideaux EBR (1928) Trans Faraday Soc 24:11
79. Lvov SN, Macdonald DD (1996) J Electroanal Chem 403:25
80. Wildgoose GG, Giovanelli D, Lawrence NS, Compton RG (2004) Electroanalysis 16:421
81. Macdonald DD, Scott AC, Wentrcek P (1979) J Electrochem Soc 126:1618
82. Oh SH, Bahn CB, Hwang IS (2003) J Electrochem Soc 150:E321
83. Minh NQ, Redey L (1987) Reference electrodes for molten electrolytes. In: Lovering DG, Gale RJ (eds) Molten salt techniques, vol 3. Plenum, New York, pp 105–287
84. Laity RW (1961) Electrodes in fused salt systems. In: Ives DJG, Janz GJ (eds) Reference electrodes. Theory and practice. Academic, New York, pp 524–606
85. Snook GA, Best AS, Pandolfo AG, Hollenkamp AF (2006) Electrochem Commun 8:1405
86. Torriero AAJ, Howlett PC (2012) Electrochem Commun 16:84
87. Rogers EI, Silvester DS, Poole DL, Aldous L, Hardacre C, Compton RG (2008) J Phys Chem C 112:2729
88. Lewandowski A, Waligora L, Galinski M (2009) Electroanalysis 21:2221
89. Sukardi SK, Zhang J, Burgar I, Horne MD, Hollenkamp AF, MacFarlane DR, Bond AM (2008) Electrochem Commun 12:250
90. Caruana DJ, McCormack SP (2001) Electrochem Commun 3:675
91. Ward KR, Freitag L, Compton RG (2010) J Phys Chem B 114:10763
92. Dickson EJF, Freitag L, Compton RG (2010) J Phys Chem B 114:187
93. Lewenstam A (2011) J Solid State Electrochem 15: 15.
94. Jasielec JJ, Filipek R, Szyszkiewicz K, Fausek J, Danielewski M, Lewenstam, A (2012) Comput Mater Sci 63: 75.
95. Zhurov K, Dickson EJF, Freitag L, Compton RG (2011) J Phys Chem B 115:6909
96. Perram JW, Stiles PJ (2006) Phys Chem Chem Phys 8:4200N10
97. Koryta J (1984) Electrochim Acta 29:445
98. Angst U, Vennesland O, Myrdal R (2009) Mater Struct 42:365
99. Lewenstam A (2007) In: Alegret S, Merkoci A (eds) Comprehensive analytical chemistry. Elsevier, Amsterdam, pp 5–24