A Method for Estimating Transport Properties of Concentrated Electrolytes from Self-Diffusion Data

Sun Ung Kim,a,b,∗ and Venkat Srinivasan,a,

aJoint Center for Energy Storage Research, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA
bRobert Bosch LLC, Research and Technology Center, Palo Alto, California 94304, USA

A theoretical method is introduced that calculates the electrolyte-transport properties using Onsager–Stefan–Maxwell (OSM) theory (concentrated-solution theory) and the generalized-Darken relation. OSM theory is used to relate binary diffusivities to the transport properties of the electrolyte, including transference number, ionic conductivity, and Fickian diffusivity. The generalized-Darken relation is proposed to calculate the binary diffusivities of multicomponent systems from self-diffusivities. Finally, an example is demonstrated to show the details of how this method can be used to estimate transport properties. The calculated properties were reasonably close to the previously reported experimental values.

© The Author(s) 2016. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0541614jes] All rights reserved.

Manuscript received September 21, 2016. Published November 4, 2016.

To develop a physics-based lithium-ion battery model or battery management systems, accurate estimation of electrolyte transport properties are essential. This is especially true as new high-energy cells are designed with thick electrodes wherein electrolyte transport dominates the end of discharge at high current densities.

However, the experimental measurements of the electrolyte properties are not trivial because it requires well-controlled experimental apparatus to obtain accurate values. Depending on the technique used, the estimation of the transport properties can be very sensitive to both natural and induced convection when estimating the diffusion coefficient. In addition, solvent reduction; inevitable when using lithium metal electrodes in electrochemical techniques, results in side reactions, and gas formation, leading to conovalent of the obtained data.1

To properly describe mass transport in a solution, a (n−1)/2 transport properties are necessary for n chemically distinct species because the system has (n−1)/2 binary diffusivities (Di,j). In a general lithium-ion battery, the electrolyte includes a cation, an anion, and a solvent; therefore, three independent transport properties are required. The cation transference number relative to the solvent τi,0, ionic conductivity κ, and Fickian diffusivity D serve to describe the mass transport of the electrolyte.

In this work, we introduced a novel method of evaluating the electrolyte-transport properties using the Onsager–Stefan–Maxwell (OSM) theory (concentrated-solution theory) combined with the generalized-Darken relation. This method provides a way to estimate transport properties with minimized experimental measurements. The key to this method is converting self-diffusivities to binary diffusivities of multicomponent systems using the generalized-Darken relation. After the conversion, OSM theory can be used to calculate the electrolyte transport properties from the binary diffusivities. This paper is intended to provide the details of this conversion and evaluate its accuracy. As an example, we demonstrate the applicability by calculating the three transport properties of LiPF6 in PC, and show that the estimated properties compare favorably with published literature data.

Onsager–Stefan–Maxwell (OSM) Theory

In multicomponent systems, the Nernst–Planck (NP) theory (dilute-solution theory) and the concentrated-solution (OSM) theory is necessary to describe the mass diffusion. To explain how the electrochemical potential is related to the relative motion of different species in multicomponent systems, however, OSM theory is more rigorous because it includes ion-ion interactions in electrolytes. This is especially true at high concentrations as the ion-ion interactions become significant.

In OSM theory, the multicomponent-mass diffusion is driven by the spatial gradient of electrochemical potential χi, and the binary diffusion is closely related to the drag coefficients of species i and j, Kij. The Stefan–Maxwell equation of N species is

\[ \vec{c}_i \cdot \nabla \mu_i = \sum_{j \neq i} K_{ij} (\vec{v}_j - \vec{v}_i) = RT \sum_{j \neq i} \frac{c_i c_j}{\nu_i \nu_j} (\vec{v}_j - \vec{v}_i), \]  

where ci is the concentration of species i, vi is the velocity of the species i, R is the universal gas constant, T is the absolute temperature, cT is the total solution concentration, and Dij is the binary diffusivity of species i and j. The binary diffusivity is another way to describe the friction between species i and j, and it is inversely proportional to the drag coefficients Kij. Equation 1 demonstrates that the relative velocity of the species is inversely proportional to the binary diffusivities Dij, but it is proportional to the binary diffusivities Dij.

In a binary electrolyte system, Equation 1 can be rearranged with the Faraday’s law

\[ \vec{i} = F \sum_i \vec{z}_i \vec{N}_i = F \left( z_e \vec{N}_+ + z_i \vec{N}_- \right) \]  

to describe the ion fluxes \( \vec{N}_i \).

\[ \vec{N}_+ = \vec{c}_+ \vec{v}_+ = -\frac{\nu_+ D \vec{v}_+}{\nu_0} + \frac{\vec{i}_0}{z_e F} + \vec{c}_+ \vec{v}_0 \]  

\[ \vec{N}_- = \vec{c}_- \vec{v}_- = -\frac{\nu_- D \vec{v}_-}{\nu_0} + \frac{\vec{i}_0}{z_e F} + \vec{c}_- \vec{v}_0 \]  

where \( \vec{c} \) is the current density, F is the Faraday constant, \( \vec{z}_i \) and \( \nu_i \) are the charge number and the stoichiometry of species i, respectively. \( \nu_0 \) is the total number of moles of ions into which a mole of electrolyte dissociates (\( \nu = \nu_+ + \nu_- \)), \( c_\mu \) is the electrochemical potential of the electrolyte (\( c_\mu = v_+ \mu_+ + v_- \mu_- \)). The local concentration of neutral salt, \( c_i \), is defined as

\[ c = \frac{c_\mu}{\nu_+} = \frac{c_\mu}{\nu_-}, \]  

the solvent concentration is

\[ c_0 = \frac{\rho_0}{M_0}, \]  

where \( \rho_0 \) is the solvent density, and \( M_0 \) is the molar mass of the solvent, and the total concentration is

\[ c_T = c_i + c_+ + c_-, \]  

\[ c_T = \frac{c_\mu}{\nu_+} + \frac{c_\mu}{\nu_-} + c_0, \]  

\[ c_T = \frac{c_\mu}{\nu_+} + \frac{c_\mu}{\nu_-} + \frac{\rho_0}{M_0}, \]  

\[ c_T = \frac{c_\mu}{\nu_+} + \frac{c_\mu}{\nu_-} + \frac{\rho_0}{M_0}. \]
The thermodynamic diffusivity of binary electrolyte is\(^4,10\)
\[ D = \frac{\nu D_{0+} D_{0-}}{\nu_{-} - D_{0+} + \nu_{+} - D_{0-}} = \frac{z_+ z_- D_{0+} D_{0-}}{z_+ D_{0+} - z_- D_{0-}}. \]  
\[ \text{[8]} \]

The thermodynamic diffusivity describes the diffusion by a chemical-potential gradient rather than by a concentration gradient. The transference numbers relative to the solvent velocity \(v_0\) are\(^4,10\)
\[ \tau_0^i = 1 - \tau_0^p = \frac{\nu_{-} - D_{0+} + \nu_+ - D_{0-}}{z_+ - D_{0+} - z_- D_{0-}}. \]  
\[ \text{[9]} \]

OSM theory also provides ionic conductivity of the solution as a function of the binary diffusivities and the transference number\(^4\)
\[ \kappa = -\frac{RT}{F^2 z_j z_{-} c_j} \left( \frac{1}{D_{y_-}} + \frac{\tau_0^j}{c_j D_{0-}} \right). \]  
\[ \text{[10]} \]

The above relation between the ionic conductivity and the binary diffusivity holds where the scale is greater than the Debye length. The thermodynamic diffusivity \(D\) is related to the Fickian diffusivity \(D_F\) by\(^6,10\)
\[ D = D_F (1 + \frac{d \ln \gamma_{y-}}{d \ln m}), \]  
\[ \text{[11]} \]

where \(\gamma_{y-}\) is the mean molal activity coefficient and \(m\) is the molality. The Fickian diffusivity \(D\) describes the diffusion by the concentration gradients.\(^15\) In the Fick's first law of diffusion, \(J = -D \nabla c\), the flux of matter \(J\) is proportional to the spatial gradient of concentration and the Fickian diffusivity \(D.\)\(^15\) The activity coefficient \(\gamma_{y-}\) determines the amplitude of concentration overpotential in electrolyte because the Fickian diffusivity depends on the activity coefficients; and, the concentration overpotential could be larger at higher currents.\(^6,10\) In order to evaluate the Fickian diffusivity with Equation 11, the thermodynamic diffusivity should be evaluated with Equation 8 in addition to obtaining the activity coefficient. Please note that if one would get the full set of the binary diffusivities of a binary electrolyte \((D_{0+}, D_{0-}, \text{and } D_{-})\), then the thermodynamic diffusivity (Equation 8), the transference numbers (Equation 9), and the ionic conductivity (Equation 10) can be calculated with OSM theory. In addition, accounting for the activity coefficient allows evaluating the Fickian diffusivities using Equation 11.

**Generalized-Darken Relation**

The key to the novel method that we introduce in the paper is implementing the generalized-Darken relation to evaluate the binary diffusivities from the self-diffusivity. Then, as we described in the previous section, the binary diffusivities can be used to calculate the three electrolyte transport properties. The traditional Darken relation\(^11\) assumed the composition dependence of the binary diffusivity in a binary system is
\[ D_{12} = x_2 D_1 + x_1 D_2, \]  
\[ \text{[12]} \]

where \(D_i\) is the self-diffusivity (or tracer diffusivity) of species \(i\), and \(x_i\) is the mole fraction of species \(i\).
\[ x_i = \frac{c_i}{c_T}. \]  
\[ \text{[13]} \]

The self-diffusivity has been measured experimentally\(^18-24\) as well as calculated numerically using MD simulations.\(^25-33\) To measure the self-diffusivity experimentally, some researchers have measured the mutual diffusion of two liquids of very nearly equal concentrations.\(^38,39\) In addition, the nuclear magnetic resonance (NMR) method has been widely used to measure the self-diffusivity.\(^20-24\) The self-diffusivity measured by NMR has been used to evaluate the transference number;\(^22-24\) however, to the best of our knowledge, only the dilute-solution theory (Einstein theory) has been used for the calculations. Previously, the NMR self-diffusivity could not be used for the calculation of the transference number in OSM theory (Equation 9) because the relation between the self-diffusivity and the binary diffusivity was not known for multicomponent systems.

In 2005, Krishna and van Baten\(^12\) introduced the following generalized-Darken relation for multicomponent systems.
\[ D_{ij} = \frac{x_i}{x_i + x_j} D_i + \frac{x_j}{x_i + x_j} D_j, \]  
\[ \text{[14]} \]

The binary diffusivity of species \(i\) and \(j\), \(D_{ij}\), is dependent on the self-diffusivities \(D_i\) and \(D_j\); however, the binary diffusivity is weighted with mole fractions of \(i\) and \(j\). Krishna and van Baten verified that the above relation is valid for of ternary and quaternary mixtures of linear alkanes by MD simulations.\(^12\) First, Krishna and van Baten evaluated the self-diffusivities of each component by the MD simulations, and then all the binary diffusivities at various compositions were evaluated by the MD simulations as well as by the generalized-Darken relation (Equation 14). Finally, two results were compared to validate the generalized-Darken relation. Krishna and van Baten showed that the generalized-Darken relation could evaluate all the binary diffusivity in their systems.

**Experimental Values and Evaluation of Transport Properties of LiPF\(_6\) in PC**

In this section, as an example, the transport properties of LiPF\(_6\) in PC were evaluated using OSM theory and the generalized-Darken relation. We selected LiPF\(_6\) in PC as a test system because the self-diffusivities, the activity coefficient and all three transport-properties (transference number, ionic conductivity, and Fickian diffusivity) have been experimentally measured and reported previously. To evaluate the transport properties, at first, the binary diffusivities were evaluated using the self-diffusivities, and then the transference number, the ionic conductivity, and the Fickian diffusivity are calculated, consecutively. Finally, the evaluated values were compared to the previously reported values.

**Binary diffusivity evaluation using self-diffusivity.**—For calculating the binary diffusivities with the generalized-Darken relation (Equation 14), the self-diffusivities are necessary. As described in the previous section, the self-diffusivities could be evaluated with MD simulations or could be measured experimentally. Takeuchi et al. measured the self-diffusivities of LiPF\(_6\) in PC by the pulse gradient spin echo (PGSE) NMR technique in the concentration range of 0.1 M to 3 M at room temperature \((T = 298 \text{ K})\).\(^23\) Figure 1 shows the self-diffusivities of cation \((D_+),\) anion \((D_-),\) and solvent \((D_0),\) respectively. The self-diffusivities decrease as its concentration increases because the ion-ion interaction becomes stronger at higher concentrations. One might think that the self-diffusivity measured by NMR might not be exactly the same as the values measured with traditional methods such as mutual diffusion measurement\(^16,19\) or MD simulations;\(^25-33\) however, the difference between NMR measurement and MD simulation was reported to be minimal.\(^34\) The aim of this article is to provide a theoretical method to evaluate the transport

![Figure 1](https://example.com/figure1.png)

**Figure 1.** The self-diffusivities of cation (□), anion (△), and solvent (□) as a function of salt concentration.\(^23\) The self-diffusivities were measured by the pulse gradient spin echo NMR technique.
properties from self-diffusivities and activity coefficients; therefore, more detailed discussion regarding the differences between the measured self-diffusivities in different methods is out of scope of the paper and will be the subject of subsequent studies.

Using the generalized-Darken relation (Equation 14) and the self-diffusivities in Figure 1, the binary diffusivities of $D_{\text{LiPF}_6}$, $D_{\text{PC}}$, and $D_{\text{Li}^+\text{PF}_6}$ are calculated as a function of the salt concentration (see Figure 2). The mole fractions $(x_i)$ at a given salt concentration are calculated through the following steps: first, we calculate the concentrations of each component, $c_+$ and $c_-$, and $c_0$ by using Equation 5 to provide the cation and anion concentrations $(c_+$ and $c_-)$ at the given salt concentrations and Equation 6 to calculate the solvent concentration $c_0$. Then, we evaluate the total concentration $c_T$ using Equation 7. Finally, we calculate the mole fractions $x_i$ by Equation 13, and apply the $x_i$ values to the generalized-Darken relation (Equation 14).

Figure 2 demonstrates the binary diffusivities, calculated from the self-diffusivities in Figure 1, and the generalized-Darken relation (Equation 14) as described above. One can see that, in general, the binary diffusivities decrease as the concentration increases, however, $D_+$ decreases faster than $D_0$ + $D_–$. This suggests that the ion-interaction is stronger at higher concentrations compared to the interaction with the solvent.

Transference numbers evaluation with the binary diffusivities.—Using the binary diffusivities in Figure 2, the transference numbers were calculated as a function of the salt concentration with Equation 9, where $z_+ = 1$ and $z_- = -1$ for LiPF$_6$ in PC. The match to the previously reported values was reasonable. Stewart and Newman$^{16}$ reported the Li$^+$ transference number of LiPF$_6$ in PC; however, the value was only measured at infinite dilution. In order to compare the calculated values at different concentrations, the transference numbers of similar chemistries were shown in Figure 3. The Li$^+$ transference number higher than 2.5 M was not available in the literature. One can see that the transference numbers up to 2 M is reasonably close to the experimental data.

Ionic conductivity calculation with the binary diffusivities.—Using the binary diffusivities in Figure 2 and the previously evaluated transference numbers (Equation 9), the ionic conductivity of LiPF$_6$ in PC has been calculated with OSM theory in Equation 10. We note that measuring the conductivity is a simple experiment and the approach outlined here is not needed in practice; however, it serves to provide a test for the accuracy of the approach. The thermodynamic diffusivity $D$ was evaluated using Equation 8 and the binary diffusivities, shown in Figure 2. The binary diffusivities were calculated with the NMR self-diffusivities as described in the previous section.

Figure 4 shows the comparison between the ionic conductivity calculated from the binary diffusivities and the previously reported experimental values of LiPF$_6$ in PC. Although the ionic conductivities are evaluated from the NMR self-diffusivities, the calculated ionic conductivities reasonably match the magnitude of the conductivity as well as how the conductivity changes over the concentration range. Both of the measured and the calculated values have the maximum concentration near 1 M, and the conductivity decreases at higher concentrations. The higher values estimated using this procedure can be attributed to lower dissociation of the salt leading to less charge carriers. While the conductivity measurement depends on the charge carrier concentration, the self-diffusivity reported using NMR tracks both the dissociated and the un-dissociated lithium in the electrolyte leading to higher values of the conductivity than reality.$^{38}$

Fickian diffusivity with the binary diffusivities and the activity coefficient.—Finally the Fickian diffusivity of LiPF$_6$ in PC was evaluated with the binary diffusivity and the activity coefficient using Equation 11. The activity coefficient was taken from a literature. Stewart and Newman measured the activity coefficient of LiPF$_6$ in PC using a concentration cell at room temperature, and reported the value:$^{16}$

$$1 + \frac{d \ln \gamma_+}{d \ln m} = c_0 \bar{V}_0 \left[ 1 + c_0 \left( -1.6934 \left( 1 - \frac{1}{\sqrt{c}} \right) - \frac{3.92}{1 + 3.92 \sqrt{c}} \right) + 1.5223 \right],$$

where $\bar{V}_0$ is the partial molar volume of the solvent. The solvent concentration $c_0$ and the total concentration $c_T$ in Equation 11 were evaluated with Equations 6 and 7. The evaluated Fickian diffusivity values are shown in Figure 5. One can see that the evaluated values were within the range of the previously reported values.$^{35,39}$
Nishida et al.\textsuperscript{30} reported the measured Fickian diffusivity of LiPF$_6$ in PC; however, the concentration range was only between 0.63 M and 0.84 M. Valøen and Reimers\textsuperscript{35} measured the Fickian diffusivity of LiPF$_6$ in PC/EC/DMC 10:27:63 in a wider concentration range 0.39 M and 3.3 M. The values were demonstrated in Figure 5 as well. One can see that the Nishida et al.’s Fickian diffusivity of LiPF$_6$ in PC were similar to Valøen and Reimers’ diffusivity of LiPF$_6$ in PC/EC/DMC.

The calculated Fickian diffusivity is comparable over the wide range of concentration. The resulting Fickian diffusivity values have similar magnitude. Not only that, we also see agreement in the trend with the diffusion coefficient decreasing with increasing concentration.

In summary, the method outlined above shows reasonable agreement with published values of ionic conductivity, cation transfer number, and Fickian diffusion coefficient on a known electrolyte system.

Step-by-Step Instruction for Calculation of Electrolyte Transport Properties

1. Step 1: using self-diffusivities, calculate binary diffusivities by the generalized-Darken relation (Equation 14).
2. Step 2: calculate transference numbers (Equation 9) from the binary diffusivity from Step 1.
3. Step 3: evaluate thermodynamic diffusivity with Equation 8, and calculate solvent concentration, and total concentration at each concentration using Equations 6 and 7.
4. Step 4: evaluate ionic conductivity (Equation 10) using the binary diffusivity from Step 1, and the thermodynamic diffusivity, the solvent and the total concentrations from Step 3.
5. Step 5: calculate Fickian diffusivity with the thermodynamic diffusivity from Step 3 and the activity coefficient from concentration cell or other methods (Equation 11).

Conclusions

A combination of concentrated-solution theory\textsuperscript{2-10} and the generalized-Darken relation\textsuperscript{11,12} was proposed to evaluate electrolyte-transport properties from self-diffusion data. An example of LiPF$_6$ in PC demonstrated that OSM theory and the generalized-Darken relation could calculate the transference number, the ionic conductivity, and the Fickian diffusivity. All three evaluated properties match the magnitude of the experimental values reasonably well. In addition, the calculated ionic conductivity and the Fickian diffusivity decreased in similar fashion as the experimental values when comparing concentrations up to 3 M.

Acknowledgments

This work was supported as part of the Joint Center for Energy Storage Research, an Energy Innovation Hub funded by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences (BES).

References

1. S. G. Stewart, Determination of Transport Properties and Optimization of Lithium Batteries, University of California at Berkeley, Thesis (2007).
2. L. Onsager, "Annals of the New York Academy of Sciences", 46, 241 (1945).
3. J. Liu and C. W. Monroe, Electrochimica Acta, 167, 357 (2015).
4. J. S. Newman and K. E. Thomas-Alvey, Electrochemical systems, 3rd ed., p. 674, Wiley-IEEE (2004).
5. E. N. Lightfoot, E. L. Cussler, and R. L. Rettig, AIChE Journal, 8, 708 (1962).
6. J. Newman, D. Bennion, and C. W. Tobias, Ber. Bunssch Ges. Phys. Chem., 69, 608 (1965).
7. R. B. Bird, W. E. Stewart, and E. N. Lightfoot, Transport Phenomena, 2nd ed., Wiley, (2001).
8. S. F. Kim, "Multicomponent Diffusion Systems, University of Michigan, Thesis", (2013).
9. A. M. Bizeray, D. A. Howey, and C. W. Monroe, J. Electrochem. Soc., 163, E223 (2016).
10. J. Newman and T. W. Chapman, AIChE Journal, 19, 343 (1973).
11. L. S. Darken, Trans. AIME, 175, 184 (1948).
12. R. Krishna and J. M. van Baten, Ind. Eng. Chem. Res., 44, 6939 (2005).
13. M. Planck, Annalen der Physik, 275, 161 (1890).
14. M. Planck, Annalen der Physik, 276, 561 (1890).
15. D. A. Fick, Philosophical Magazine Series 4, 10, 30 (1855).
16. S. Stewart and J. Newman, J. Electrochem. Soc., 155, A458 (2008).
17. S. F. Kim and C. W. Monroe, Applied Energy, 103, 207 (2013).
18. D. L. Bidlack and D. K. Anderson, J. Phys. Chem., 68, 206 (1964).
19. J. J. C. Sheikh and P. A. Lyons, J. Phys. Chem., 73, 3258 (1969).
20. M. Helbæk, B. Hafskjold, D. K. Dythe, and G. H. Sørland, J. Chem. Eng. Data, 41, 598 (1996).
21. Y. Saito et al., Journal of Power Sources, 81-82, 772 (1999).
22. J. Zhao, L. Wang, X. He, C. Wan, and C. Jiang, J. Electrochem. Soc., 155, A292 (2008).
23. M. Takeuchi et al., Journal of Molecular Liquids, 148, 99 (2009).
24. M. Kliet et al., J. Am. Chem. Soc., 134, 14654 (2012).
25. I. M. J. J. Van de Ven-Lucassen, T. J. H. Vlugt, A. J. J. Van der Zanden, and P. J. A. M. Kerkhof, Mol. Phys., 94, 495 (1998).
26. D. K. Dythe, A. H. Fuchs, B. Rousseau, and M. Durandeau, The Journal of Chemical Physics, 110, 4060 (1999).
27. G. H. Goo, G. Sang, S. H. Lee, and T. Change, Bulletin of the Korean Chemical Society, 23, 1595 (2002).
28. D. R. Wheeler and J. Newman, J. Phys. Chem. B, 108, 18353 (2004).
29. D. R. Wheeler and J. Newman, J. Phys. Chem. B, 108, 18362 (2004).
30. D. J. Keffer and P. Adhangale, Chemical Engineering Journal, 100, 51 (2004).
31. G. A. Fernández, J. Vrabec, and H. Hasse, International Journal of Thermophysics, 25, 175 (2004).
32. G. A. Fernández, J. Vrabec, and H. Hasse, Int J Thermophys., 26, 1389 (2005).
33. N. N. Rajput, X. Qu, N. Sa, A. K. Burrell, and K. A. Persson, J. Am. Chem. Soc., 137, 3411 (2015).
34. K. S. Han et al., J. The Chemical Physics, 141, 104509 (2014).
35. L. G. Valøen and J. N. Reimers, J. Electrochem. Soc., 152, A882 (2005).
36. Y. Ashara et al., J. Electrochem. Soc., 151, A119 (2004).
37. M. Doyle and Y. Fuentes, J. Electrochem. Soc., 159, A706 (2003).
38. K. Hayamizu, J. Chem. Eng. Data, 57, 2012 (2012).
39. T. Nishida, K. Nishikawa, and Y. Fukunaka, ECS Trans., 6, 1 (2008).

Figure 5. The Fickian diffusivities as a function of concentration and the comparison to the previously reported experimental values (■: this work, □: Nishida et al. (PC at T = 294 K)\textsuperscript{35} and ( ): Valøen and Reimers (PC/EC/DMC 10:27:63)\textsuperscript{35}). The evaluated Fickian diffusivity has the same order as the previously reported values, and the diffusivities decrease as the concentration increases.