

CHAPTER OVERVIEW

10: Electrolyte Solutions

The thermodynamic properties of electrolyte solutions differ in significant ways from the properties of mixtures of nonelectrolytes.

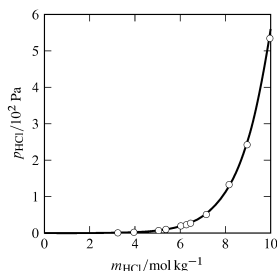


Figure 10.1 Partial pressure of HCl in a gas phase equilibrated with aqueous HCl at 25 °C and 1 bar. Open circles: experimental data from Stuart J. Bates and H. Darwin Kirschman, *J. Am. Chem. Soc.*, **41**, 1991–2001, 1919.

Here is an example. Pure HCl (hydrogen chloride) is a gas that is very soluble in water. A plot of the partial pressure of gaseous HCl in equilibrium with aqueous HCl, as a function of the solution molality (Fig. 10.1), shows that the limiting slope at infinite dilution is not finite, but zero. What is the reason for this non-Henry's law behavior? It must be because HCl is an electrolyte—it dissociates (ionizes) in the aqueous environment.

It is customary to use a *molality* basis for the reference and standard states of electrolyte solutes. This is the only basis used in this chapter, even when not explicitly indicated for ions. The symbol μ_{+}° , for instance, denotes the chemical potential of a cation in a standard state based on molality.

In dealing with an electrolyte solute, we can refer to the solute (a substance) as a whole and to the individual charged ions that result from dissociation. We can apply the same general definitions of chemical potential, activity coefficient, and activity to these different species, but only the activity coefficient and activity of the solute as a whole can be evaluated experimentally.

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