Topic 0485

Chemical Potentials, Composition and the Gas Constant

In many Topics describing the thermodynamic properties of liquid mixtures and solutions, key equations relate the chemical potentials of components to the composition of a given system. For example in the case of a binary aqueous mixture the chemical potential of water $\mu_1(T, p, mix)$ is related to the mole fraction of water x_1 at temperature T and pressure p using equation (a).

$$\mu_1(T, p, mix) = \mu_1^*(T, p, \ell) + R \cdot T \cdot \ln(x_1 \cdot f_1) \quad \text{(a)}$$

By definition, $\text{limit}(x_1 \rightarrow 1) f_1 = 1.0$ (b)

Here $\mu_1^*(T, p, \ell)$ is the chemical potential of water (ℓ) at the same T and p; f_1 is the rational activity coefficient of water in the mixture.

Similarly for solute j in an aqueous solution at temperature T and pressure p, the chemical potential of solute j, $\mu_j(T, p, aq)$ is related to the molality m_j using equation (c) where $m^0 = 1$ mol kg^{-1}.

$$\mu_j(aq, T, p) = \mu_j^0(aq, T, p) + R \cdot T \cdot \ln(m_j \cdot \gamma_j / m^0) \quad \text{(c)}$$

By definition, at all T and p $\text{limit}(m_j \rightarrow 0)\gamma_j = 1.0$ (d)

Here $\mu_j^0(aq, T, p)$ is the chemical potentials of solute j in an aqueous solution at the same T and p where $m_j = 1.0$ mol kg^{-1} and $\gamma_j = 1.0$.

In equations (a) and (c) the parameter R is the Gas Constant, 8.314 J mol^{-1} K^{-1}. The word 'Gas' in the latter sentence is interesting bearing in mind that equations (a) and (c) describe the properties of liquids, mixtures and solutions. Here we examine how this parameter emerges in these equations.

The starting point is a description of a closed system containing i–chemical substances, the amount of chemical substance j being n_j.

Then, $G = G[T, p, n_i]$ (e)

The chemical potential $\mu_j(T, p)$ of chemical substance j is given by equation (f).

$$\mu_j(T, p) = \left(\frac{\partial G}{\partial n_j}\right)_{T, p, n(i \neq j)} \quad \text{(f)}$$

Moreover the partial molar volume V_j of chemical substance j is given by equation (g).

$$V_j = \left(\frac{\partial \mu_j}{\partial p}\right)_T \qquad \text{(g)}$$

We simplify the argument by considering a system comprising pure chemical substance 1.

Then $$V_1^* = \left(\frac{\partial \mu_1^*}{\partial p}\right)_T \qquad \text{(h)}$$

Thus $V_1^*(T, p)$ is the molar volume of pure substance 1 at temperature T and pressure p.

In the event that chemical substance 1 is a perfect (ideal) gas, the following equation describes the p-V-T properties.

$$p_1^* \cdot V_1^*(g) = R \cdot T \qquad \text{(i)}$$

We write equation (h) in the following form describing an ideal gas at constant temperature T.

$$d\mu_1^*(g) = V_1^*(g) \cdot dp \qquad \text{(j)}$$

Equations (i) and (j) yield equation (k).

$$d\mu_1^*(g) = R \cdot T \cdot d\ln p_1^* \qquad \text{(k)}$$

We integrate equation (k) between limits p_1^* and p^0 where p^0 is the standard pressure, 101325 N m^{-2}.

Hence, at temperature T, $\mu_1^*(g;T;p_1^*) = \mu_1^*(g;T;p^0) + R \cdot T \cdot \ln(p_1^* / p^0)$ (l)

In a more complicated system, the gas phase is a gaseous mixture, comprising two components, component 1 and component 2 with partial pressures p_1 and p_2. We assume the thermodynamic properties of the gas phase in equilibrium with a liquid phase are ideal. Hence equation (l) takes the following form where $\mu_1(g;mix;p_1)$ is the chemical potential of gas-1 at partial pressure p_1.

$$\mu_1^{eq}(g;mix;id;T;p_1) = \mu_1^*(g;T;p^0) + R \cdot T \cdot \ln(p_1^{eq} / p^0) \qquad \text{(m)}$$

Liquid Mixtures

A given closed system contains chemical substances 1 and 2, present in two phases, gas and a liquid mixture at temperature T and pressure p. Thus p_1^{eq} is the equilibrium partial pressure of chemical substance 1 in the gas phase. At equilibrium the chemical potentials of chemical substance 1 in the vapour and liquid mixture phases are equal.

$$\mu_1^{eq}(\ell;mix;id;p;T) = \mu_1^{eq}(g;mix;T;p_1^{eq}) \qquad \text{(n)}$$

Thus p_1^{eq} is the partial pressure of chemical substance 1 in the gas phase, the superscript 'eq' indicating an equilibrium with the liquid phase at pressure p; the complete system is at temperature T.

Hence using equations (m) and (n) we obtain an equation for the equilibrium chemical potential of chemical substance 1 in an ideal liquid mixture at temperature T and pressure p

$$\mu_1^{eq}(\ell; mix; id; p; T) = \mu_1^*(g; p^0; T) + R \cdot T \cdot \ln(p_1^{eq} / p^0) \qquad (o)$$

The thermodynamic analysis calls on the results of experiments in which the partial pressure p_i of chemical substance-i in a liquid mixture at temperature T is measured as a function of mole fraction x_i. It turns out that for nearly all liquid mixtures at fixed temperature, p_i is approximately a linear function of the mole fraction x_1 at low x_1. We therefore define an ideal liquid mixture. By definition the (equilibrium) vapour pressure of chemical substance i, one component of a liquid mixture, is related to the mole fraction composition at temperature T using equation (p).

Thus $$p_i^{eq}(T; mix; id) = x_i \cdot p_i^*(\ell; T) \qquad (p)$$

Here x_i is the mole fraction of component-i in the liquid mixture; $p_i^*(\ell; T)$ is the vapour pressure of pure liquid substance 1 at temperature T.

For example if x_i is 0.5, the contribution to the vapour pressure of the (ideal) mixture is one-half of the vapour pressure of the pure liquid-i at the same temperature. Equation (p) is Raoult's law, describing the properties of an ideal liquid mixture having ideal thermodynamic properties. We note that the Gas Constant emerges in equation (o) because the r.h.s. of equation (o) describes the properties of chemical substance 1 in the vapour phase.

Combination of equations (o) and (p) yields equation (q).

$$\mu_i^{eq}(\ell; mix; id; T; p) = \mu_i^*(g; T; p^0) + R \cdot T \cdot \ln[x_i \cdot p_i^*(T) / p^0] \qquad (q)$$

Or, $$\mu_i^{eq}(\ell; mix; id; p; T) = \mu_i^*(g; p^0; T) + R \cdot T \cdot \ln[p_i^*(T) / p^0] + R \cdot T \cdot \ln(x_i) \qquad (r)$$

For the pure liquid-i at pressure p,

$$\mu_i^*(\ell; p; T) = \mu_i^*(g; p^0; T) + R \cdot T \cdot \ln[p(T) / p^0] \qquad (s)$$

Hence, $$\mu_i^{eq}(\ell; mix; id; p; T) = \mu_i^*(\ell; p; T) + R \cdot T \cdot \ln(x_i) \qquad (t)$$

We notice that the Gas Constant in equation (t) emerged from equation (i) describing the properties of an ideal gas.

Solutions

A similar argument is used when we turn our attention to the thermodynamic properties of a solute, chemical substance j. In this case we use Henry's Law as the link between theory and the properties of solutions. This law relates the equilibrium partial pressure p_j of solute j to the molality of solute j, m_j for a solution at temperature T and pressure p . Experiment shows that certainly for dilute solutions, the partial pressure p_j is close to a linear function of molality m_j. Taking this experimental result as a lead we state that, by definition, in the event that the thermodynamic properties of the solution are ideal, equation (u) relates the partial pressure p_j to the solute molality m_j ; $m^0 = 1\ \text{mol kg}^{-1}$.

Thus, $p_j(s\ln;T;m_j;id) = H_j \cdot (m_j / m^0)$ (u)

Here H_j is Henry's Law constant characteristic of solute, solvent, T and p. H_j is a pressure being the partial pressure of solute j where $m_j = 1\,\text{mol kg}^{-1}$. In other words equation (u) is not thermodynamic in the sense of being derived from the Laws of Thermodynamics. Rather the basis is experiment. We return to equation (n) but written for the equilibrium for solute in solution and in the vapour phase, a mixture of solute j and solvent.

$$\mu_j^{eq}(s\ln;m_j;T;p) = \mu_j^{eq}(g;mix;T;p_j^{eq}) \qquad \text{(v)}$$

For the vapour phase, $\mu_j^{eq}(g;mix;T;p_j^{eq})$ is related to the partial pressure p_j^{eq} using equation (w).

$$\mu_j^{eq}(g;mix;T;p_j^{eq}) = \mu_j^0(g;T;p^0) + R \cdot T \cdot \ln(p_j^{eq} / p^0) \qquad \text{(w)}$$

Hence using equations (u)-(w),

$$\mu_j^{eq}(s\ln;m_j;T;p) = \mu_j^0(g;T;p^0) + R \cdot T \cdot \ln\left[\frac{H_j}{p^0} \cdot \frac{m_j}{m^0}\right] \qquad \text{(x)}$$

Or, $\mu_j^{eq}(s\ln;m_j;T;p) = \{\mu_j^0(g;T;p^0) + R \cdot T \cdot \ln\left[\frac{H_j}{p^0}\right]\} + R \cdot T \cdot \ln(m_j / m^0)$ (y)

The term $\{\mu_j^0(g;T;p^0) + R \cdot T \cdot \ln\left[\frac{H_j}{p^0}\right]\}$ characterises solute j in a solution at the same T and p when $m_j = 1\,\text{mol kg}^{-1}$. Thus we define a reference chemical potential for the solute-j, $\mu_j^0(s\ln;T;p)$ as given by $\{\mu_j^0(g;T;p) + R \cdot T \cdot \ln\left[\frac{H_j}{m_j^0}\right]\}$. (z)

Therefore, $\mu_j^{eq}(s\ln;m_j;T;p) = \mu_j^0(s\ln;T;p) + R \cdot T \cdot \ln(m_j / m^0)$ (za)

Again we can trace the gas constant R in equation (za) to a description of the vapour state although the term $\mu_j^{eq}(s\ln; m_j; T; p)$ describes the chemical potential of chemical substance j, the solute, in solution.

Finally we should note that for real as opposed to ideal liquid mixtures and ideal solutions, activity coefficients express the extent to which the properties of these systems differ from those defined as ideal.