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TEACHING ACTIVITIES AND ACTIVITY COEFFICIENTS: AN ALTERNATIVE APPROACH

Jamil Ahmad
University of Botswana (Botswana)

Abstract. The article outlines an approach to teaching the concept of activity and activity coefficient starting with the relationship between Gibbs free energy change and pressures of ideal gases for the process of their mixing. The gases are then assumed to be the vapor in equilibrium with a liquid solution, allowing concentrations in the solution to be related to the vapor pressures through Raoult's or Henry's laws, appropriately modified to account for any deviation from these laws. Chemical potentials of individual components of the liquid solution are then related to activities, and the expression for the equilibrium constant in terms of activities is developed.

Keywords: activity; activity coefficient; equilibrium constant; Raoult's law, Henry's law; chemical potential

Introduction

The topic of activity and activity coefficient is among the more challenging ones in an undergraduate physical chemistry curriculum. A common approach is to first introduce fugacity of a gas and define a standard state (Laidler et al., 2003). Activity is then defined as the ratio of fugacity to fugacity at the standard state. Another approach is to use the expression for chemical potential of a constituent gas of a reaction mixture expressed in terms of the chemical potential at a standard state and the pressure of the gas. This equation is then applied to solutions by retaining its form (Klotz & Rosenberg, 2008; Atkins & de Paula, 2001). In order for this equation to be valid for solutions, the term that replaces pressure is called activity.

An alternative procedure to develop activity is described here. This development requires that by way of background students should be familiar with Gibbs free energy calculations, particularly for the process of expansion of an ideal gas. The other essential concepts are the partial molar quantities, specifically chemical potential, and its role in phase equilibrium. All of these concepts are usually covered in a physical chemistry course before activities are introduced. This development avoids the introduction of fugacity, and also gives a clearer physical meaning to activity.

The need for defining activity

The Gibbs free energy of a reaction system is an important quantity, which can give information about the direction of the reaction or if the system is at equilibrium. Equilibrium constant of a system can be calculated from partial molar Gibbs free energy values of reactants and products in their standard states. Activity is a quantity that allows calculation of the partial molar Gibbs free energy values.

The development of activity function can be understood if we first consider a system in which all the reactants and products are ideal gases. For such a reaction, partial pressures of the constituent gaseous reactants are all that we need in order to calculate the Gibbs free energy change, ΔG, since it is relatable to pressure. This can be done by using simple thermodynamic relations developed in an introductory course as shown in the following section. What does one do for a solution? It would be useful to have an analogous measureable quantity that can be used for solutions, just as pressure is used for a gaseous system. Activity is such a quantity. The transition from gas mixture to solutions can be made if the two phases are in equilibrium. In that case the chemical potential of a substance is the same in both phases.

Gibbs free energy of mixing of ideal gases

We imagine two ideal gases, A and B, contained in separate vessel of volumes $V\neg\neg_{\mathrm{A}}$ and V_{B} respectively, as shown in Fig 1, both at a constant temperature T. The quantities of the gases are, respectively, n_{A} and n_{B} moles. The two gases constitute the system.

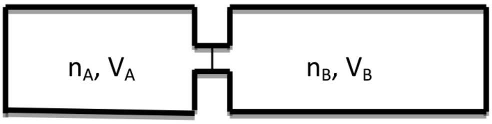

Figure 1. Gases A and B confined in volumes V_{A} and $V_{\mathrm{B},}$ which are allowed to mix

Now consider what happens when the gases are allowed to mix. The temperature, T, remains constant. The process is akin to each gas expanding from its initial volume, V_{A} or V_{B} to a final volume ($V\neg\neg_{\mathrm{A}} + V_{\mathrm{B}}$). For the gas A, the free energy change, ΔG_{A}, on mixing will be given by: $\Delta G_{\mathrm{A}} = n_{\mathrm{A}}RT \ln [V\neg\neg_{\mathrm{A}} / (V\neg\neg_{\mathrm{A}} + V_{\mathrm{B}})]$, and similarly for the gas B. For the whole process of mixing, the change in Gibbs energy is given by:

$$\Delta G_{\mathrm{mix}} = n_{\mathrm{A}}RT \ln [V\neg\neg_{\mathrm{A}}/(V\neg\neg_{\mathrm{A}} + V_{\mathrm{B}})] + n_{\mathrm{B}}RT \ln [V\neg\neg_{B}/(V\neg\neg_{\mathrm{A}} + V_{\mathrm{B}})]. \quad (1)$$

For the two gases, the initial Gibbs energy before the process of mixing is: $G_{\mathrm{A}} = n_{\mathrm{A}}\ G_{\mathrm{A}}*$, and $G_{\mathrm{B}} = n_{\mathrm{B}}\ G_{\mathrm{B}}*$, where $G_{\mathrm{A}}*$, $G_{\mathrm{B}}*$ are the values of the Gibbs energy for

1 mol of the pure gas. The Gibbs energy for the mixture can be written in terms of the partial molar Gibbs energy of each constituent gas, and is given by: $G_{\text{final}} = n_A \bar{G}_A + n_B \bar{G}_B$.

Here $\bar{G}_A$ and $\bar{G}_B$ are the partial molar free energies of the two gases in the final mixture. The Gibbs energy change for the system as the result of the process of mixing is then,

$$\Delta G_{\text{mix}} = (n_A \bar{G}_A + n_B \bar{G}_B) - (n_A G_A{}^* + n_B G_B{}^*). \tag{2}$$

This is clearly the same ΔG_{mix} as given in Eq (1) above. Equating the two expressions for ΔG_{mix} as given in Eq (1) and Eq (2), we get $n_A RT \ln [V_A/(V_A + V_B)] + n_B RT \ln [V\neg\neg_B/(V\neg\neg_A + V_B)] = (n_A \bar{G}_A + n_B \bar{G}_B) - (n_A G_A{}^* + n_B G_B{}^*)$.

Since n_A and n_B are arbitrary, their coefficients on both sides of the equation must be equal. We have, then: $n_A \bar{G}_A - n_A G_A{}^* = n_A RT \ln [V_A/(V_A + V_B)]$.

Recalling that $\bar{G}_A$ is the chemical potential, μ_A, of the gas A in the mixture, and $G_A{}^*$ is the chemical potential, $\mu_A{}^*$, of the pure gas, we can rewrite the above equation as: $n_A\mu_A = n_A\mu_A{}^* + n_A RT \ln [V_A/(V_A + V_B)]$, which, on dividing by $n_{A,}$ simplifies to: $\mu_A = \mu_A{}^* + RT \ln [V_A/(V_A + V_B)]$.

According to the Boyle's Law for ideal gases, at constant temperature, the initial volume of each gas divided by the final volume equals the ratio of the final partial pressure (P_A) to the initial, or the pressure of the pure gas, ($P_A{}^*$). Or, $[V_A/(V_A + V_B)] = P_A / P_A{}^*$. This gives: $\mu_A = \mu_A{}^* + RT \ln (P_A /P_A{}^*)$, and $\mu_B = \mu_B{}^* + RT \ln (P_B / P_B{}^*)$.

In any mixture of ideal gases, then, the chemical potential of each component is given by:

$$\mu_i = \mu_i{}^* + RT \ln (P_i /P_i{}^*) \tag{3}$$

Now suppose the two gases arose as vapor in equilibrium with a solution of the substances A and B. Since the vapor pressures of liquids in a mixture normally encountered are low enough the vapor behaves as an ideal gas. Thus, there is no need to introduce the fugacity function, which is needed for non-ideal gases. At equilibrium, the chemical potential of the component, i, in the liquid solution, μ_i^{LIQ}, equals the chemical potential of the same substance in the vapour phase. Thus, for the substance i in the liquid and the vapor phase, $\mu_i^{\text{LIQ}} = \mu_i^{\text{vap}}$; μ_i^{vap} is the μ_i of Eq (3).

Eq (3) can then be written as

$$\mu_i^{\text{LIQ}} = \mu_i{}^* + \mathrm{RT} \ln (\mathrm{P}_i / \mathrm{P}_i{}^*) \tag{4}$$

If the solution obeys Raoult's law, $P_i/P_i^* = X_{i.}$ Here P_i = vapour pressure of the component i and P_i^* is the vapour pressure of the pure substance i. X_i is the mole fraction of the component i in the solution. Eq (3) becomes, on substitution of the Raoult's law equation:

$$\mu_i^{\mathrm{LIQ}} = \mu_i^{*} + \mathrm{RT}\ln \mathrm{X}_{i.} \tag{5}$$

For non-ideal solutions, i.e. when the solution does not obey Raoult's law, this equation is not valid. To account for this non-ideality, a factor Υ_i, called activity coefficient, has to be introduced. The vapor pressure of the component i at each concentration, instead of being given by the Raoult's law equation, is given by: $P_i/P_i^* = \Upsilon_i X_{i.}$

For solutions not obeying Raoult's law, instead of Eq. (5), the following equation applies: $\mu_i^{\mathrm{LIQ}} = \mu_i^{*} + RT\ln \Upsilon_i X_{i.}$

Since all the terms in this equation apply to the liquid phase, we can dispense with the superscript LIQ, and rewrite the equation as:

$$\mu_i = \mu_i^{*} + \mathrm{RT}\ln \Upsilon_i \mathrm{X}_{i..} \tag{6}$$

Activity of the component i in the solution is defined as $a_i = \Upsilon_i \mathrm{X}_i$. This gives us:

$$\mu_i = \mu_i^{*} + RT\ln a_i \tag{7}$$

and

$$P_i/P_i^* = \Upsilon_i X_i = a_i. \tag{8}$$

Activity of a pure substance

From Eq. (6) or Eq. (7), it is evident that the activity of a pure substance is 1, since $\mu_i = \mu_i^{*}$. Similarly, by Eq. (7), if in a reaction system a pure solid or liquid is present, its activity is unity, since its vapor pressure, P_i^*, is unaffected by what else is present in the system.

Derivation of equilibrium constant expression

The expression of equilibrium constant can be derived in terms of activity. As an example we consider the isomerization reaction propene ⇌ cyclopropane. For simplicity, we represent it as p⇌c. The total Gibbs fee energy of a reaction mixture consisting of the two gases is given by $G = n_p \bar{G}_p + n_c \bar{G}_c = n_p \mu_p + n_c \mu_c$. At equilibrium G is a minimum, implying that at that stage an infinitesimally small fluctuation in the amount of either one of the reactants will not change total G. In other words, $\mathrm{d}G = 0$.

Thus by differentiation of the preceding equation, we get:

$$\mathrm{d}G/\mathrm{d}n_p = \mu_p + (\mathrm{d}n_c/\mathrm{d}n_p).\mu_{c.} = 0 \tag{9}$$

Since a decrease in the number of moles of propene results in an increase in moles of cyclopropane, $\mathrm{d}n_c = -\,\mathrm{d}n_p$, $(\mathrm{d}n_c/\mathrm{d}n_p) = -1$.

Eq. (9) becomes, $\mathrm{d}G/\mathrm{dn}_p = \mu_p - \mu_{c.} = 0$.

Substituting Eq. (7) in the above, we get: $[(\mu_c^* + RT \ln a_c) - (\mu_p^* + RT \ln \mathrm{a}_p)] = 0$; $\mu_c^* - \mu_p^* = -RT \ln (a_c/a_p)$. Since μ^* values are simply the respective Gibbs free energies per mole for the two pure components, this can be written as: $\bar{G}_c^* - \bar{G}_p^* = \Delta G^* = -RT \ln K$, where $K = a_c/a_{p.}$

The preceding equations define the equilibrium constant, *K,* in terms of the activities or reactants and products.

This treatment can be extended to the general case of chemical reaction: $\mathrm{p}P + \mathrm{q}Q \rightleftharpoons \mathrm{r}R + \mathrm{s}S$.

The equilibrium constant for this reaction can be written in terms of the activities of each reactant P, Q, R and S and the respective stoichiometric coefficient.

$$\mathrm{K} = (\mathrm{a}_R^{\,r} \times \mathrm{a}_S^{\,s})/(\mathrm{a}_P^{\,p} \times \mathrm{a}_Q^{\,q}) \tag{10}$$

If a reactant is a pure liquid or a solid, its activity is unity, and so it need not be included in the expression (Ahmad, 2016).

Activities based on Henry's law

In the preceding development of relation between chemical potential of a component in solution and its concentration, advantage has been taken of the Raoult's law to extend to the solution phase what applies to the gas phase. For solutions whose behavior deviates from Raoult's law, activity coefficient has been introduced to take into account this deviation. What if this deviation is very large as for a solute in a dilute solution? It turns out that in dilute solutions, the vapor pressure of solutes can be related to concentration through Henry's law: $P = k_H.m$. where m is the concentration of the component i per kg of the solvent, and the Henry's law constant, k_H, is constant for a particular system at a constant temperature.

Using this in Eq. (3), we get: $\mu_i = \mu_i^* + RT \ln (k_H.m / P_i^*) = \mu_i^* + RT \ln (k_H/P_i^*) + RT \ln m_i$.

For the solutions obeying Henry's law for the solute, this can be put in the following form by replacing the first two terms on the right hand with a quantity $\mu_i^{*\prime}$: $\mu_i = \mu_i^{*\prime} + RT \ln m_i$.

Clearly $\mu_i^{*'}$ is the chemical potential of the component i in the solution at m =1, if Henry's law is followed. If there is deviation from Henry's law, an activity coefficient has to be introduced as in the case of the Raoult's law. This gives: $\mu_i = \mu_i^{*'} + RT \ln \Upsilon_i'; m_i = \mu_i^{*'} + \mathrm{RT} \ln a_i'$.

The state of the solution where $a_i' = \Upsilon_i' m_i = 1$ is known as the standard state for the component i. This is the hypothetical state where m =1 and the solution follows Henry's law. Activity coefficient based on Henry's law are called rational activity coefficients.

A treatment similar to the one for activities based on Raoult's law can be used to get the equilibrium constant expression analogous to Eq. (10).

Conclusion

The more familiar and accessible expression of the chemical potential of a component in a gas mixture in terms of partial pressures has been put in a form applicable to solutions by using Raoult's law for making the connection. For solutions obeying Raoult's law the expression uses mole fractions. For those deviating from Raoult's law activities are used. A similar treatment can be carried out if the solution obeys Henry's law or deviates somewhat from it.

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✉ **Prof. Jamil Ahmad**
Department of Chemistry
University of Botswana
Private Bag 00704, Gaborone, Botswana
E-mail: ahmadj@mopipi.ub.bw