

17.5: Partial and Mean Molar Quantities

Consider a single phase with several components. Suppose there are N_i moles of component i , so that the total number of moles of all species is

$$N = \sum N_i. \quad (17.5.1)$$

The *mole fraction* of species i is

$$n_i = \frac{N_i}{N}, \quad (17.5.2)$$

and of course $\sum n_i = 1$.

Let V be the volume of the phase. What will be the increase in volume of the phase if you add dN_i moles of component i at constant temperature and pressure? The answer, of course, is

$$dV = \left(\frac{\partial V}{\partial N_i} \right)_{T,P,N_j} dN_i \quad (17.5.3)$$

If you increase the number of moles of all species at constant temperature and pressure, the increase in volume will be

$$dV = \sum \left(\frac{\partial V}{\partial N_i} \right)_{T,P,N_j} dN_i. \quad (17.5.4)$$

The quantity $\left(\frac{\partial V}{\partial N_i} \right)_{T,P,N_j}$ is called the *partial molar volume* of species i :

$$v_i = \left(\frac{\partial V}{\partial N_i} \right)_{T,P,N_j} \quad (17.5.5)$$

Let us suppose that the volume of a phase is just proportional to the number of moles of all species in the phase. It might be thought that this is always the case. It would indeed be the case if the phase contained merely a mixture of ideal gases. However, to give an example of a non-ideal case: If ethanol C_2H_5OH is mixed with water H_2O , the volume of the mixture is less than the sum of the separate volumes of water and ethanol. This is because each molecule has an electric dipole moment, and, when mixed, the molecules attract each other and pack together more closely than in the separate liquids. However, let us go back to the ideal, linear case.

In that case, if a volume V contains N moles (of all species) and you add N_i moles of species i at constant temperature and pressure, the ratio of the new volume to the old is given by

$$\frac{V + dV}{V} = \frac{N + dN_i}{N}, \quad (17.5.6)$$

and hence

$$\frac{dV}{V} = \frac{dN_i}{N}, \quad (17.5.7)$$

or

$$\left(\frac{\partial V}{\partial N_i} \right)_{P,T,N_j} = v_i = \frac{V}{N}. \quad (17.5.8)$$

Example. (You'll need to think long and carefully about the next two paragraphs fully to appreciate what are meant by *molar volume* and *partial molar volume*. You'll need to understand them before you can understand more difficult things, such as partial molar Gibbs function.)

A volume of 6 m^3 contains 1 mole of A, 2 moles of B and 3 moles of C. Thus the *molar volumes* (not the same thing as the partial molar volumes) of A, B and C are respectively 6, 3 and 2 m^3 .

Assume that the mixing is *ideal*. In *that case*, equation 17.5.8 tells us that the partial molar volume of each is the total volume divided by the total number of moles. That is, the *partial molar volume* of each is 1 m^3 . You could imagine that, before the component were mixed (or if you were to reverse the arrow of time and un-mix the mixture), we had 1 mole of A occupying 1 m^3 , 2 moles of B occupying 2 m^3 and 3 moles of C occupying 3 m^3 , the molar volume of each being 1 m^3 .

The *mean molar volume per component* is

$$\bar{v} = \frac{V}{N}. \quad (17.5.9)$$

If the components are ideal, each component has the same partial molar volume, and hence the mean molar volume is equal to the partial molar volume of each – but this would not necessarily be the case for nonideal mixing.

The total volume of a phase, whether formed by ideal or nonideal mixing, is

$$V = \sum N_i v_i. \quad (17.5.10)$$

If you divide each side of this equation by N , you arrive at

$$\bar{v} = \sum n_i v_i. \quad (17.5.11)$$

Note that the partial molar volume of a component is not just the volume occupied by the component divided by the number of moles. I.e. the partial molar volume is not the same thing as the molar volume. In our ideal example, the molar volume of the three components would be, respectively, 6, 3 and 2 m^3 .

Another way of looking at it: In the mixture, N_i moles of species i occupies the entire volume V , as indeed does every component, and its *molar volume* is V/N_i . The pressure of the mixture is P . Now remove all but species i from the mixture and then compress it so that its pressure is still P , it perforce must be compressed to a smaller volume, and the volume of a mole *now* is its *partial molar volume*.

Let Φ be any extensive quantity (such as S , V , U , H , A , G).

Establish the following notation:

Φ = total extensive quantity for the phase;

ϕ_i = partial molar quantity for component i ;

$\bar{\phi}$ = mean molar quantity per component.

The partial molar quantity ϕ_i for component i is defined as

$$\phi_i = \left(\frac{\partial \Phi}{\partial N_i} \right)_{P, T, N_{j \neq i}}. \quad (17.5.12)$$

The total value of Φ is given by

$$\Phi = \sum N_i \phi_i, \quad (17.5.13)$$

and the mean value per component is

$$\bar{\phi} = \sum n_i \phi_i. \quad (17.5.14)$$

If the extensive quantity Φ that we are considering is the Gibbs function G , then equation 17.5.12 becomes

$$g_i = \left(\frac{\partial G}{\partial N_i} \right)_{P, T, N_{j \neq i}} \quad (17.5.15)$$

Then we see, by comparison with equation 17.4.28 that the *chemical potential* μ_i of component i is nothing other than its partial molar Gibbs function.

Note that this is not just the Gibbs function per mole of the component, any more than the partial molar volume is the same as the molar volume.

Recall (Chapter 14 on the Clausius-Clapeyron equation) that, when we had just a single component distributed in two phases (e.g. a liquid in equilibrium with its vapour), we said that the condition for thermodynamic equilibrium between the two phases was that the specific or *molar Gibbs functions* of the liquid and vapour are equal. In Section 17.5 of this chapter, when we are dealing with several components distributed between two phases, the condition for chemical equilibrium is that the *chemical potential* μ_i of component i is the same in the two phases. Now we see that the chemical potential is synonymous with the partial molar Gibbs function, so that the condition for chemical equilibrium between two phases is that the partial molar Gibbs function of each component is the same in each phase. Of course, if there is just one component, the partial molar Gibbs function is just the same as the molar Gibbs function.

Although pressure is an intensive rather than an extensive quantity, and we cannot talk of “molar pressure” or “partial molar pressure”, opportunity can be taken here to define the *partial pressure* of a component in a mixture. The partial pressure of a component is merely the contribution to the total pressure made by that component, so that the total pressure is merely

$$P = \sum p_i, \quad (17.5.16)$$

where p_i is the partial pressure of the i th component,

Dalton's Law of Partial Pressures states that for a mixture of ideal gases, the partial pressure of component j is proportional *mole fraction* of component j . That is, for a mixture of ideal gases,

$$\frac{p_j}{P} = \frac{p_j}{\sum p_i} = \frac{N_j}{N} = \frac{N_j}{\sum N_i} = n_j. \quad (17.5.17)$$

That is,

$$p_j = n_j P. \quad (17.5.18)$$

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