

Partial molar property



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INTRODUCTION

A partial molar property is the contribution (per mole) that a substance makes to an overall property of a mixture. The easiest partial molar property to visualize is the partial molar volume, v_j of a substance j the contribution j makes to the total volume of a mixture. we can see that although 1 mol of a substance has a characteristics volume when it is pure, 1 mol of that substance can make different contributions to the total volume of a mixture because molecules pack together in different ways in the pure substance and in mixture.

the partial molar volume at an intermediate composition of the waterethanol mixture is an indication of the volume the H₂O molecules occupy when they are surrounded by a mixture of molecules representative of the overall composition(half water, half ethanol) for instance. when the molar fraction are both 0's.

The partial molar volume, V_J , of any substance J at a general composition, is defined as:

where the subscript n' indicates that the amount of all the other substances is held constant.

The partial molar is the slope of the plot of the total volume as the amount of J is changed with all other variables held constant:

it is quite possible for the partial molar volume to be negative, as it would be at II in the above diagram. For example, the partial molar volume of magnesium sulphate in water is $-1.4 \text{ cm}^3 \text{ mol}^{-1}$. i. e. addition of 1 mol

MgSO₄ to a large volume of water results in a decrease in volume of 1.4 cm³. (The contraction occurs because the salt breaks up the open structure of water as the ions become hydrated.)

Once the partial molar volumes of the two components of a mixture at the composition and temperature of interest are known, the total volume of the mixture can be calculated from:

The expression may be extended in an analogous fashion to mixtures with any number of components.

The most common method of measuring partial molar volumes is to measure the dependence of the volume of a solution upon its composition. The observed volume can then be fitted to a function of the composition (usually using a computer), and the slope of this function can be determined at any composition of interest by differentiation.

PARTIAL MOLAR GIBBS ENERGY

The most useful partial molar quantity is the partial molar free energy G_i , pm. It is so useful that it is given the name of chemical potential and a separate symbol μ_i . The chemical potential is just another name for the partial molar Gibbs energy. For a substance in a mixture, the chemical potential is defined as being the partial molar Gibbs energy:

i. e. the chemical potential is the slope of a plot of the Gibbs energy of the mixture against the amount of component J, with all other variables held constant:

In the above plot, the partial molar Gibbs energy is greater at I than at II.

The total Gibbs energy of a binary mixture is given by:

where the sum is across all the different substances present in the mixture, and the chemical potentials are those at the composition of the mixture.

This indicates that the chemical potential of a substance in a mixture is the contribution that substance makes to the total Gibbs energy of the mixture.

In general, the Gibbs energy depends upon the composition, pressure and temperature. Thus G may change when any of these variables alter, so for a system that has components A, B, etc, it is possible to rewrite the equation $dG = Vdp - SdT$ (which is a general result that was derived here) as follows:

The idea that the changing composition of a system can do work should be familiar – this is what happens in an electrochemical cell, where the two halves of the chemical reaction are separated in space (at the two electrodes) and the changing composition results in the motion of electrons through a circuit, which can be used to do electrical work.

it is possible to use the relationships between G and H , and G and U , to generate the following relations:

Now $H = U + PV$

To measure partial molar volumes

There are several ways that partial molar volumes can be measured. One way is to begin with one mole of a compound, call it component 1, add a small amount of component 2 and measure the volume, add a little more of component 2 and measure the volume again. Keep doing this until the

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desired concentration range has been covered. Then fit the volume data to a curve, for example, of the form,

The constants, a , b , c , etc are obtained from the curve fitting and the first term is the molar volume of pure component 1. Then the partial molar volume of component 2 can be obtained by direct differentiation,

Ideal Solutions

We will define an ideal solution as a solution for which the chemical potential of each component is given by,

where μ_i is the chemical potential of pure component i , and X_i is the mole fraction of component i in the solution.

where p_i^* is the vapor pressure of pure component i .)

We have to prove that an ideal solution obeys Raoult's law (using definition).

Consider a solution of two components where the mole fraction of component 1 is X_1 . We know that the chemical potential of component 1 must be the same in the solution as in the vapor in equilibrium with the solution. That is,

Equation 10 doesn't help us very much all by itself. However we have some more information. We know that for the pure component 1 we have $X_1 = 1$, and we know that the pressure of component 1 vapor in equilibrium with the liquid is just the vapor pressure of the pure liquid, p_1^* , so that,

which is Raoult's law.

[5]Chemical potential of an ideal gas

the chemical potential μ of an ideal gas at a given temperature is related to its pressure p through eq.

$$\mu = \mu^\circ + RT \ln(p/p^\circ) \quad (15)$$

where μ° is the standard chemical potential when the pressure of the gas is p° ,

equation 15 suggest that at a given temperature, the pressure of the gas is a measure of its chemical potential. if inequalities in pressure exist in a gas container, the gas flows spontaneously from the high pressure region to the lower pressure region until the pressure is equalized throughout the vessel. In the later stage, the gas has the same value of chemical potential throughout the container.

IMPORTANCE OF CHEMICAL POTENTIAL

The chemical potentials are the key properties in chemical thermodynamics. the μ_i determine reaction equilibrium and phase equilibrium. Moreover, all other partial molar properties and all thermodynamics properties of the solution can be found from the μ_i ' s

APPLICATIONS

Partial molar properties are useful because chemical mixtures are often maintained at constant temperature and pressure and under these conditions, the value of any extensive property can be obtained from its partial molar property. They are especially useful when considering specific

properties of pure substances (that is, properties of one mole of pure substance) and properties of mixing.

$$\Delta_{\text{mix}} H \equiv H - H^*, \Delta_{\text{mix}} S \equiv S - S^*, \Delta_{\text{mix}} G \equiv G - G^*$$

Where H , S and G are properties of the solutions and H^* , S^* , and G^* are properties of the pure unmixed components at the same T and P as the solution.

the key mixing quantity is $\Delta_{\text{mix}} G = G - G^*$. The Gibbs energy G of the solution is

$G = \sum_i G_i$ (where G_i is a partial molar quantity). The Gibbs energy G^* of the unmixed components is $G^* = \sum_i G_i^*$, (where G_i^* is the molar Gibbs energy of pure substance i). Therefore

$$\Delta_{\text{mix}} G \equiv G - G^* = \sum_i (G_i - G_i^*) \text{ const } T, P \quad (1)$$

which is similar for $\Delta_{\text{mix}} V$. we have

$$\Delta_{\text{mix}} G = \Delta_{\text{mix}} H - T \Delta_{\text{mix}} S \text{ const } T, P \quad (2)$$

which is a special case of $\Delta G = \Delta H - T \Delta S$ at constant T .

$\Delta_{\text{mix}} S$ and $\Delta_{\text{mix}} V$ can be found as partial derivatives of $\Delta_{\text{mix}} G$. Taking (T, n_j) of eq(1), we have

$$\left(\frac{\partial \Delta_{\text{mix}} G}{\partial T} \right)_{T, n_j} = \sum_i (G_i - G_i^*) - T \sum_i \left(\frac{\partial G_i}{\partial T} - \frac{\partial G_i^*}{\partial T} \right)_{T, n_j} -$$

$$\sum_i (V_i - V_i^*)_{T, n_j}$$

$$\left(\frac{\partial \Delta_{\text{mix}} G}{\partial n_j} \right)_{T, n_j} = \Delta_{\text{mix}} V \quad (3)$$

The changes $\Delta_{\text{mix}}V$, $\Delta_{\text{mix}}U$, $\Delta_{\text{mix}}H$, $\Delta_{\text{mix}}C_p$ that accompany solution formation are due entirely to changes in intermolecular interactions (both energetic and structural). However, changes in S , A and G result not only from changes in intermolecular interactions but also from the unavoidable increase in entropy that accompanies the constant T and P mixing of substance and the simultaneous increase in volume each component occupies. Even if the intermolecular interactions in the solution are the same as in the pure substances, $\Delta_{\text{mix}}S$ and $\Delta_{\text{mix}}G$ will still be non zero.

GIBBS- DUHEM EQUATION

A relation that imposes a condition on the composition variation of the set of chemical potentials of a system of two or more components, where S is entropy, T absolute temperature, P pressure, n_i the number of moles of the i th component, and μ_i is the chemical potential of the i th component. Also known as Duhem's equation.

Deriving the Gibbs-Duhem equation for volume. The total differential of the Gibbs free energy in terms of its natural variables is

With the substitution of two of the Maxwell relations and the definition of chemical potential, this is transformed into:

the chemical potential is just another name for the partial molar (or just partial, depending on the units of N) Gibbs free energy, thus

The total differential of this expression is

Subtracting the two expressions for the total differential of the Gibbs free energy gives the Gibbs-Duhem relation:

FUGACITY

The presences of molecular interactions distinguish the real gases from ideal gases where the molecular interactions are completely absent. For a real gas $V_m \neq RT/P$ and hence $d\mu \neq RT d \ln P$. Since the ideal gas equations are not directly applicable to real gases, we are faced with a problem. We can either sacrifice the equations or the variable. If we abandon the general equation of chemical potential then we have to use various equation of state fitting with P-V-T data. The use of such equations of state will make the treatment more complicated. So we find it easier to retain the general form of the chemical potential and to define a new variable which has the dimensions and general properties of pressure. The new variable is called the fugacity, which is derived from the Latin fugere, to flee, and means literally 'escaping tendency'. It is denoted by f . it is a corrected pressure which applies to real gases. all the effects arising due to interactions are contained in f .

the chemical potential of a pure real gas can be expressed in a form

$$\mu = \mu_0 + RT \ln(f/atm)$$

μ_0 is the standard chemical potential at unit fugacity.

at very low pressure . the ratio $(f/p) = \gamma$ is called the fugacity coefficient. for an ideal gas $f = p$ and the fugacity coefficient is unity.

with this definition of the fugacity we may now express the chemical potential as:

$$\mu = \mu_0 + RT \ln(\gamma P/atm) = \mu_0 + RT \ln(P/atm) + RT \ln \gamma$$

on comparing this expression with that for an ideal gas [$\mu_{\text{ideal}} = \mu_0 + RT \ln(P/\text{atm})$]

Condition of fugacity of a gas

Let us consider the relation $d\mu = V_m dP$

$$d\mu = V_m(\text{ideal})dP \text{ and } d\mu(\text{real}) = V_m(\text{real}) dP$$

Let us consider a change in the state of the system from an initial pressure P' to a final pressure P , and let f' be the fugacity of the real gas at pressure P' and f the fugacity at pressure P . Integration of the expression for chemical potential yields

$$d\mu(\text{ideal}) = m(\text{ideal})dP$$

$$\text{or } \mu(\text{ideal}) - \mu'(\text{ideal}) = m(\text{ideal})dP$$

$$\text{and } \mu(\text{real}) - \mu'(\text{real}) = m(\text{real})dP$$

but for an ideal gas the chemical potential is given by

$$\mu(\text{ideal}) = \mu_0(\text{ideal}) + RT \ln(P/\text{atm})$$

$$\mu'(\text{ideal}) = \mu_0(\text{ideal}) + RT \ln(P'/\text{atm})$$

μ_0 is the standard chemical potential.

$$\mu(\text{ideal}) - \mu'(\text{ideal}) = RT \ln(P/P') = m(\text{ideal})dP \quad (1)$$

For the real gas $\mu(\text{real}) = \mu_0(\text{real}) + RT \ln(f/\text{atm})$

$$\text{and } \mu'(\text{real}) = \mu_0(\text{real}) + RT \ln(f'/\text{atm})$$

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$$\mu(\text{real}) - \mu'(\text{real}) = RT \ln(f/\text{atm}) - RT \ln(f'/\text{atm})$$

$$= RT \ln(f/f') = m(\text{ideal})dP \quad (2)$$

Taking the difference of equation (2) and (1), we get

$$RT \ln(f/f') - RT \ln(P/P') = m(\text{real}) - V_m(\text{ideal})dP$$

$$\text{or } RT \ln(f/P) - RT \ln(f'/P') = m(\text{real}) - V_m(\text{ideal})dP \quad (3)$$

$$\text{where } = V_m(\text{ideal}) - V_m(\text{real})$$

now, = +

$$RT \ln(f/p) - RT \ln(f'/P') = - + \quad (4)$$

If the pressure P' is very low then the gas will behave ideally and for this condition

$V_m(\text{ideal}) \approx V_m(\text{real})$ and $= 1$, The second term on left side and right side of equation (4) will be equated to zero, therefore

$$RT \ln(f/P) = -$$

$$\text{or } \ln(f/P) = -1/RT$$

Antilogarithm gives

$$(f/P) = \exp$$

$$\text{or } f = P \exp($$

$$= P \exp[V_m(\text{real}) - V_m(\text{ideal})]dP \quad (5)$$

SUMMARY

we had covered in this term paper about partial molar properties one important thing is The properties of a solution are not additive properties, it means volume of solution is not the sum of pure components volume. When a substance becomes a part of a solution it loses its identity but it still contributes to the property of the solution. The term partial molar property is used to designate the component property when it is a mixture with one or more component solution.

the most important partial molar quantity is the partial molar free energy it is an intensive property because it is a molar quantity. it is denoted by μ_i . now we also know that how to measure the partial volume. and then the ideal solution is the solution in which the components in pure form here we take the pure components of chemical potential . then the applications of partial molar property is the property of mixing which is very useful. it is defined in term paper

and the important concept Gibbs duhem equation A relation that imposes a condition on the composition variation of the set of chemical potentials of a system of two or more components

physical significance is that if the composition varies, the chemical potentials do not change independently but in a related way. and then included fugacity another important part of partial molar properties. The fugacity f plays the role of pressure and need not be equal to the actual pressure of the real gas.

RESULT

The overall result is the partial molar property is not of all about pure components. The term partial molar property is used to designate the component property when it is a mixture with one or more component solution. and also find out the chemical potential other name of gibbs energy and about ideal gases, fugacity.