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# MOIST GASES. THERMODYNAMIC PROPERTIES

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## Moist Gases: Thermodynamic Properties

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Fundamental laws of thermodynamics of solutions and of the molecular-kinetic theory of gases and liquids serve as the basis of an original technique for constructing equations of state and employing the latter for calculating thermodynamic properties of moist gases over the range of parameters of practical importance. Original experimental data on the solubility of ice and water in compressed pure gases are analyzed and systematized, and computer programs and algorithms are worked out for calculating tables of thermodynamic properties of moist gases simultaneously with estimation of the accuracy of results. Tables of the equilibrium mass fraction of water vapor and its thermodynamic properties (specific volume, enthalpy, entropy, specific heat at constant pressure, partial pressure of the water vapor, mass- and absolute moisture content) are calculated in a form convenient for practical use for twelve moist gases (air, nitrogen, oxygen, methane, hydrogen, helium, neon, argon, krypton, xenon, carbon dioxide and ethane) at 200 to 400 K and relative moisture content from 0 to 1 at pressures to 10 MPa.

## CONTENT

General information from thermodynamics of solutions. Ordinary water. Thermodynamic properties. Moist gases. Equations of state. Calculation of thermodynamic properties of moist gases and estimate of the uncertainty of the calculated values. Tables of thermodynamic properties of moist gases.

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Fundamental laws of thermodynamics of solutions and of the molecular-kinetic theory of gases and liquids serve as the basis of an original technique for constructing equations of state and employing the latter for calculating thermodynamic properties of moist gases over the range of parameters of practical importance.

Experimental data on the thermodynamic properties and data on the solubility of ice and water are analyzed for three groups of substances – solvents of ice and water – air and its principal constituents, hydrogen and monatomic gases, and also principal hydrocarbon gases (methane and ethane). Computer programs and algorithms for calculating tables of thermodynamic properties of moist gases coupled with estimation of the accuracy of results are worked out.

The equations derived in the book are employed for calculating tables of the equilibrium mass fraction of water vapor and its thermodynamic properties (specific volume, enthalpy, entropy, specific heat at constant pressure, partial pressure of the water vapor, mass- and absolute moisture content) in a form convenient for practical use for twelve moist gases (air, nitrogen, oxygen, methane, hydrogen, helium, neon, argon, krypton, xenon, carbon dioxide and ethane) at 200 to 400 K and relative moisture content from 0 to 1 at pressures to 10 MPa.

The book is intended for experts in the field of chemical technology, energetics, cryogenic engineering and other industries, scientific workers, higher-degree candidates, students of energetics and chemical technology institutions of higher learning.

Knowledge of properties of substances and materials and of their specific features are the basis of the art of engineering and of scientific forecasting.

Thermodynamic properties and equations of state for binary systems from the point of view of fundamental laws of thermodynamics of solutions and the molecular-kinetic theory of gases and liquid are discussed in the book

## MOIST GASES. THERMODYNAMIC PROPERTIES

V. A. Rabinovich and V. G. Beketov

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### Intended Readership

Experts in the field of chemical technology, energetics, cryogenic engineering and other industries, scientific workers, graduate students, students involved in experimental and analytic investigations of thermodynamic properties of solutions.

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# INTRODUCTION

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The rapid advances in modern science and engineering depend directly on the availability of reliable information on the properties of various individual substances and their mixtures, that participate in given processes. It can be definitely stated that not a single scientific or engineering calculation is possible without data on properties of substances and materials. For this reason the increasingly rising needs of science and technology widen the gap between the need for reliable data and the feasibility of actually obtaining them.

The primary source of information is reliable experimentation, however, the experimental determination of handbook data over a wide range of parameters of state and compositions is very difficult, and in a number of cases simply impossible. It should be added that the formulation and conduct of experiments is highly work consuming and expensive, whereas the data that are obtained are to one or another degree fragmentary. This situation has stimulated the development of analytic methods of correlation of data on properties of substances and materials and prediction of these properties. In the case when the experimental and numerical results are equivalent with acceptable accuracy, the latter become more preferable for use in various engineering calculations and also in systems of computer design and control of industrial processes.

The absence of a comprehensive theory, which would allow predicting properties of substances from elementary principles with sufficient accuracy gave birth to a large number of empirical methods for investigating properties of substances. Such methods are of definite practical importance, but are "blind" by nature and, as a rule, cannot be used for extrapolating properties past the limits of parameters in which the input data were presented. A more fruitful path consists in efficiently combining the pragmatic advantages of empirical methods with the underlying theoretical results. When doing this, it becomes possible to quite consistently systematize and correlate experimental



results and to obtain reliable correlations even in the case of very limited body of such results. The effectiveness of the method increases when it is extended to a certain group of substances with typical characteristic attributes.

Moist gases may be regarded as belonging to such a group. All of them consist of binary systems with water vapor serving as one of the constituents. Under certain conditions the vapor may fully or partially condense, becoming liquid or crystalline. The limiting content of water vapor in the mixture is characterized by the equilibrium fraction content, which depends uniquely on the specified temperature and pressure of the mixture. It should be noted in conjunction with this that dry gases do not exist in nature. All the substances surrounding us are in the state of phase equilibrium or tend to it.

The thermodynamic state of moist gases is defined by any three independent parameters, for example, temperature, pressure and composition of the mixture. The last parameter is one of the characteristics of the moisture content. In addition to it, one frequently makes use of concepts such as the absolute moisture content, relative moisture content and degree of saturation. Precise definition of these characteristics of moist gases allows establishing unique relationships between them.

The field of practical application of moist gases is rather wide. They participate in drying and air conditioning, in the manufacture and processing of various materials, in solving specific problems in metrology, biology, medicine, meteorology, agriculture, in the food, chemical and other industries. Data on thermodynamic properties are utilized in: designing economic, highly efficient and safe processes in cryogenic engineering, developing technologies for the transportation and storage of agricultural products, optimizing chemical technology processes and equipment.

In spite of this, no specialized handbook is available in Russia or in the West which would collect, systematize and correlate data on thermodynamic processes of moist gases over the entire range of independent parameters of practical importance. The only exception is moist air, for which tables of thermodynamic properties are available, but only at atmospheric pressures and above zero temperatures.

The present book comes to fill this void. Its structure becomes obvious from its content. It starts by briefly presenting information from the thermodynamics of solutions.

The main purpose of the first chapter is to prove that the equation of state of moist gas and the equation of solubility of water and ice in a gas have the same form. This chapter also examines and analyzes all the possible phase equilibria in the binary system over the selected range of parameters of state.

In general moisture may be present in moist gases in three states: as a vapor, liquid and crystal. In the second chapter equations of state which transmit, with accuracy of modern experimentation, these properties up to the corresponding phase equilibrium curves are obtained for each of these states. Special attention is paid to these curves, since they control to a large measure the accuracy of calculation of the equilibrium fractional content of water vapor in the mixture. These equations serve for calculating the thermodynamic properties of water vapor at 200 to 400 K and pressures from zero to the corresponding values along the phase equilibrium (sublimation and saturation curves).

The third chapter is central to the book and is concerned with application of the above methods for determining the virial coefficients of the equations of state for the

twelve moist gases. The description of general approaches to solution of this problem is the content of the first twelve sections (3.1–3.12) of this chapter. This treatment implements a principle combining simultaneous utilization of original experimental data with the underlying results of the molecular-kinetic theory of gases and liquids.

The structure of all the sections of this chapter is the same. Each section shows by way of examples the implementation of the previously obtained methods of correlation of input data and obtaining final analytic equations incorporating specifics of each of the moist gases under study. This is done in most detail for moist air (Section 3.1). The material for other moist gases is given in more compact form, but not as compact as to infringe upon the independence of each subsequent section, which contains virtually the entire information that is needed on the given question.

The fourth chapter presents equations for calculating the principal thermodynamic properties of moist gases, an overall schematic diagram of such a calculation and equations for estimating the uncertainty of the final results. This was done on the assumption that the results of measurements or calculations as such are not valuable without a metrologically validated estimation of their accuracy. For this reason this problem was afforded all the necessary attention, with the result that all the predicted thermodynamic quantities have a confidence interval of uncertainty that follows from all the preceding estimations of the latter obtained at each preliminary stage of calculations.

Tables of the equilibrium mass fraction of water vapor and of its thermodynamic properties (specific volume, enthalpy, entropy, specific heat at constant pressure, partial pressure of the water vapor, mass- and absolute moisture content) in a form convenient for practical use were calculated for twelve moist gases (air, nitrogen, oxygen, methane, hydrogen, helium, neon, argon, krypton, xenon, carbon dioxide and ethane) at 200 to 400 K and relative moisture content from 0 to 1 at pressures to 10 MPa.

Every effort was exerted to make the book as convenient as possible to the readers. For this reason each chapter and section were made, as far as possible, independent of one another. A bibliography is provided at the end of each chapter. A reference can be repeated, if necessary, from one chapter to another. Although the symbols used are standard in thermophysics, we deemed it necessary to list, in the beginning of the book, the designators of all the symbols and their definitions, to make it easier for nonspecialists to use the book.

The book is intended for use in engineering practice, particularly in working out processes and equipment of the chemical technology, cryogenic engineering and other industries. It can also be useful to a wide circle of scientists, higher-degree candidates and students of energetics and chemical technology institutions of higher learning, since its content is closely related to the molecular-kinetic theory of gases and liquids and to results of utilization of this theory.

In preparing this book the authors had to overcome great difficulties, consisting in developing programs and algorithms for calculating the thermodynamic properties of moist gases and estimating the uncertainty of the predicted values. We were greatly assisted in this work by M. D. Rogovin, senior staff member of the All-Russian Research Institute of Materials and Substances, to whom we are very thankful. Thanks are also extended to candidates of engineering sciences P. V. Popov and A. V. Semenov, staff

members of this Center, who constantly extended assistance in preparing the manuscript for publication.

The assumed structure of the book followed from our desire to find, within the intended scope, an optimum compromise between the traditional forms of scientific monographs and handbooks. For this reason we limited ourself, for each gas, to the most necessary input information, which would allow, after processing, obtaining sufficiently reliable analytic expressions and to calculate the tables. The simplifications which became necessary from time to time under this approach did not seriously infringe upon the rigour and accuracy of the final equations of state for the moist gases. Still, the authors are left with a feeling that not everything came out the way it was intended. Most likely, some shortcomings will be noticed by the intended readership and we will be grateful to those who would communicate these to us and share with us their opinions and concerns.

Moscow, April 1993

*V. Rabinovich*  
*V. Beketov*

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# NOMENCLATURE

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## List of frequently encountered symbols<sup>†</sup>

Symbol	Name of quantity
$T$	absolute temperature
$t$	temperature on the Celsius scale
$p$	pressure
$p_s$	pressure of saturated of vapor above a crystal or liquid
$p_{st}$	standard pressure (101.325 kPa)
$p_0$	infinitesimal pressure
$n_i$	number of moles of the $i$ th constituent of the moist gas
$x_i$	molal fraction of the $i$ th constituent of the moist gas
$x$	molal fraction of water vapor in the moist gas
$x_{eq}$	equilibrium molal fraction of water vapor in the moist gas
$R$	universal gas constant
$V$	total volume of the system (moist gas)
$v$	molal volume of the moist gas

---

<sup>†</sup> Partial quantities are designated by an overbar.

List of frequently encountered symbols<sup>†</sup>

(Continued)

Symbol	Name of quantity
$v_i$	molal volume of the $i$ th constituent of the moist gas
$G$	Gibbs energy of the system (moist gas)
$g$	molal Gibbs energy of the moist gas
$g_i$	molal Gibbs energy of the pure $i$ th constituent of the moist gas
$\mu_i$	chemical potential of the $i$ th constituent of the moist gas
$h$	molal enthalpy of the moist gas
$h_i$	molal enthalpy of the pure $i$ th constituent of the moist gas
$c_p$	molal specific heat at constant pressure of the moist gas
$c_{p,i}$	molal specific heat at constant pressure of the $i$ th constituent of the moist gas
$S$	entropy of the system (moist gas)
$s$	molal entropy of the moist gas
$s_i$	molal entropy of the $i$ th constituent of the moist gas
$s_T^0$	standard molal entropy of the substance
$f$	fugacity
$f_i(p, T)$	fugacity of the pure $i$ th constituent of the moist gas
$f_i(p, T, x)$	fugacity of the $i$ th constituent in the moist gas
$z$	compressibility factor
$B$	second virial coefficient
$C$	third virial coefficient
$B_{11}$ and $C_{111}$	virial coefficients of the solvent gas
$B_{22}$ and $C_{222}$	virial coefficients of the water vapor
$B_{12}$ , $C_{112}$ and $C_{122}$	mixed virial coefficients
$u$	intermolecular interaction potential
$\sigma$ and $\epsilon$	parameters of the intermolecular interaction potential
$N_A$	Avogadro number
$k$	Boltzmann constant
$\sigma_{11}$ and $(\epsilon/k)_{11}$	parameters of the Lennard-Jones (6-12) potential for the solvent gas

<sup>†</sup> Partial quantities are designated by an overbar.

List of frequently encountered symbols<sup>†</sup>

(Continued)

Symbol	Name of quantity
$\sigma_{22}$ , $(\varepsilon/k)_{22}$ and $t_{22}^*$	parameters of the Stockmayer potential for water vapor
$\sigma_{12}$ , $(\varepsilon/k)_{12}$ , $\sigma_{112}$ and $(\varepsilon/k)_{112}$	mixed parameters of the Lennard-Jones (6-12) potential for the moist gas
$A_0(T)$ and $A_1(T)$	temperature functions of the equation of state of condensed water
$F$	any quantity desired in parametric form
$b_j$	$j$ th parameter of quantity $F$
$n_j$ and $q_j$	power exponents of $F$
$S$	functional being minimized
$N$	number of original experimental points
$m$	number of parameters in $F$
$s^2$	residual variance
$F_j$	significance of the $j$ th term of parametric relationship
$F_r$	significance of the regression as a whole
$\sigma$	overall <i>rms</i> uncertainty
$\sigma_w$	weighed <i>rms</i> uncertainty
$\Delta_F$	absolute uncertainty of $F$
$\delta_F$	relative uncertainty of $F$

<sup>†</sup> Partial quantities are designated by an overbar.

## SUPERSCRIPTS

0	ideal-gas state
'	condensed state at the phase equilibrium curve
"	gaseous state at the phase equilibrium curve

## SUBSCRIPTS

$i$	number of constituents of the moist gas
1	solvent gas
2	water (water vapor)
id	ideal-gas state
g	gaseous state
cond	condensed state
liq	liquid state

c	crystal state
H	crystalline hydrate
mix	mixture
m	at the melting curve
tr	in the triple point
cr	in the critical point

## REDUCED (NONDIMENSIONALIZED) QUANTITIES

$\theta = T/T_{tr}$ , $\tau = T/100 \text{ K}$ , $T^* = kT/\varepsilon$	temperature
$\pi = p/p_{tr}$	pressure
$\bar{c}_p = c_p/R$	reduced specific heat at constant pressure
$\bar{r} = r/RT_{tr}$	reduced heat of sublimation
$B_{LJ}^*$ and $C_{LJ}^*$	second and third virial coefficients of the Lennard-Jones (6-12) potential
$B_{Sh}^*$	second virial coefficient of the Stockmayer potential

## GENERAL INFORMATION FROM THERMODYNAMICS OF SOLUTIONS

Thermodynamics of solutions is the topic of a large number of textbooks and monographs, such as those by Kirilin et al. [1.1], Krichevskiy [1.2], Landau and Lifshits [1.3]. These books describe in detail various aspects of thermodynamics of multicomponent systems. The principal relationships governing phase equilibria are explored, problems related to solubility of substances in different states of the matter are analyzed and methods of calculating the thermodynamic properties of solutions are presented.

In this chapter we shall analyze only those principal concepts and relationships of thermodynamics of binary systems, which shall be utilized for obtaining specific analytic equations needed for calculating the thermodynamic properties of moist gases at temperatures from 200 to 400 K and pressures from 0.1 to 10 MPa. Phase diagrams of moist gases will be analyzed also in basically the same range of parameters.

All the extensive properties such as the volume, entropy, enthalpy, Gibbs energy, etc., will be referred to one mole of the system.

### 1.1 PARTIAL QUANTITIES

A moist gas is a binary system consisting of  $n_1$  moles of the gas that serves as the solvent and  $n_2$  moles of water vapor, which shall be treated as the second constituent. The term molal fraction of water vapor will be applied to the ratio of the number of its moles to the total number of moles in the solution:

$$x_2 = n_2 / (n_1 + n_2) \quad (1.1)$$



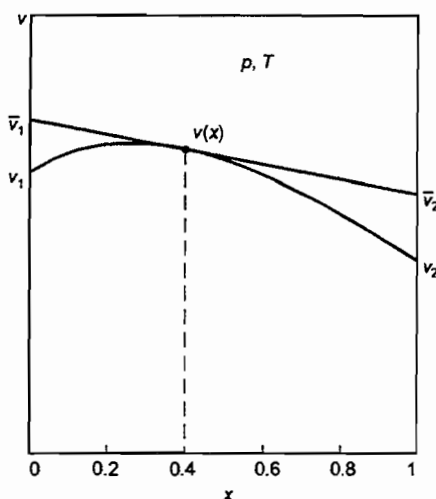


Figure 1.1 Graphical determination of partial volumes of the constituents of a binary system at specified  $p$  and  $T$ .

Similarly the molal fraction of the solvent gas will be the ratio

$$x_1 = n_1 / (n_1 + n_2) \quad (1.2)$$

According to Eqs. (1.1) and (1.2) we have

$$x_1 + x_2 = 1 \quad (1.3)$$

Consequently, only one of the fractions will be independent. Henceforth the term moist-gas fraction (fractional content) will be applied to the molal fraction of water vapor and it will be designed as  $x$  without the subscript, whereas the molal fraction of the solvent gas expressed by Eq. (1.3) will be designated as  $1 - x$ . This means that the composition of a moist gas is uniquely given by fraction  $x$  of the water vapor.

The molal volume of the moist gas

$$v = V / (n_1 + n_2) \quad (1.4)$$

and its other extensive thermodynamic properties, referred to one mole of the solution, are functions of the pressure, temperature and fractional content of vapor in the moist gas. In the range of pressure and temperatures in which the gas and the water are in the gaseous state at the same  $p$  and  $T$  and mix in one another in any ratios, the dependence of the molal volume on the molal fraction of the water vapor is depicted by the continuous curve shown in Fig. 1.1. The molal volume  $v(p, T, x)$  at  $x = 0$  and  $x = 1$  is equal respectively to the molal volumes  $v_1$  and  $v_2$  of the pure first and second constituents.

The tangent constructed in an arbitrary point on the figure cuts off points  $\bar{v}_1$  and  $\bar{v}_2$  on axes  $x = 0$  and  $x = 1$ . Quantities  $\bar{v}_1$  and  $\bar{v}_2$  are termed the partial molal volumes of the first and second constituent of the system. Their values can, by construction, be calculated from the expressions

$$\left. \begin{aligned} \bar{v}_1 &= v(p, T, x) - (\partial v / \partial x)_{p, T} x \\ \bar{v}_2 &= v(p, T, x) + (\partial v / \partial x)_{p, T} (1 - x) \end{aligned} \right\} \quad (1.5)$$

whereas the molal volume of the moist gas can be expressed in terms of the partial volumes of its constituents as

$$v(p, T, x) = \bar{v}_1(p, T, x) (1 - x) + \bar{v}_2(p, T, x) x \quad (1.6)$$

The partial molal volumes of the constituents are functions of pressure, temperature and of the molal fraction of the water vapor and have a specific physical meaning, which will become clear by approaching the definition of a partial quantity in a somewhat different manner. Defining the molal volume as per Eq. (1.4) and employing the expression

$$\frac{n_1}{n_2} = \frac{1 - x}{x} \quad (1.7)$$

and replacing the variable of differentiation, we obtain

$$\left. \begin{aligned} \left( \frac{\partial v}{\partial x} \right)_{p, T} &= \frac{v}{x} - \frac{1}{x} \left( \frac{\partial V}{\partial n_1} \right)_{p, T, n_2} \\ \left( \frac{\partial v}{\partial x} \right)_{p, T} &= \frac{1}{1 - x} \left( \frac{\partial V}{\partial n_2} \right)_{p, T, n_1} - \frac{v}{1 - x} \end{aligned} \right\} \quad (1.8)$$

Substitution of Eqs. (1.8) into (1.5) yields the following equations for the partial volumes of the constituents:

$$\bar{v}_1 = \left( \frac{\partial V}{\partial n_1} \right)_{p, T, n_2} \quad \bar{v}_2 = \left( \frac{\partial V}{\partial n_2} \right)_{p, T, n_1} \quad (1.9)$$

This means that the partial volume of a constituent in a solution at specified  $p$ ,  $T$  and  $x$  is none other than the increment of the total volume of the solution, devolving upon a single mole of this constituent when it is added to the solution at unchanged  $p$ ,  $T$  and amount of the second constituent.

At constant pressure and temperature the volume, as other extensive properties of the system, is a function of the molal content of the constituents. For this reason the differential of the total volume at constant  $p$  and  $T$ .

$$dV_{p, T} = \left( \frac{\partial V}{\partial n_1} \right)_{p, T, n_2} dn_1 + \left( \frac{\partial V}{\partial n_2} \right)_{p, T, n_1} dn_2 \quad (1.10)$$

or

$$dV_{p,T} = \bar{v}_1 dn_1 + \bar{v}_2 dn_2 \quad (1.11)$$

If both constituents are added to the solution at constant  $p$  and  $T$  in proportions such that the composition does not change, then the partial volumes of the constituents as functions of  $p$ ,  $T$  and  $x$  remain unchanged. Then the integral of Eq. (1.11) is

$$V = \bar{v}_1 n_1 + \bar{v}_2 n_2 \quad (1.12)$$

Differentiating now Eq. (1.12) at constant  $p$  and  $T$ ,

$$dV_{p,T} = \bar{v}_1 dn_1 + n_1 d\bar{v}_1 + \bar{v}_2 dn_2 + n_2 d\bar{v}_2 \quad (1.13)$$

and equating Eqs. (1.11) and (1.13), we obtain

$$n_1 d\bar{v}_1 + n_2 d\bar{v}_2 = 0 \quad (1.14)$$

or

$$(1-x)d\bar{v}_1 + xd\bar{v}_2 = 0 \quad (1.15)$$

Equation (1.14) is known as the Gibbs-Duhem equation. It allows obtaining a relationship between the equations expressing the fractional content dependence of the partial constituent volumes at constant pressure and temperature by differentiating Eq. (1.15) with respect to the molal fraction:

$$\frac{(\partial\bar{v}_1/\partial x)_{p,T}}{(\partial\bar{v}_2/\partial x)_{p,T}} = -\frac{x}{1-x} \quad (1.16)$$

The partial fractions of the constituents of a binary system can be calculated from Eq. (1.5) provided that the thermal equation of state of the system can be solved for the volume, i.e., if the expression for  $v(p, T, x)$  is known. If the equation of state cannot be solved for the volume, as, for example, is the case of the virial equation, but can be solved for the pressure, then it becomes difficult to calculate the partial volumes from Eqs. (1.5). In this case it is much more convenient to evaluate the derivative of the molal fraction of the water vapor not with respect to the volume, but to pressure. To obtain the necessary expressions, we write the differential of the pressure as a function of the system's volume and its water vapor fraction:

$$dp = \left(\frac{\partial p}{\partial v}\right)_{T,x} dv + \left(\frac{\partial p}{\partial x}\right)_{T,v} dx \quad (1.17)$$

whence

$$\left(\frac{\partial v}{\partial x}\right)_{p,T} = -\frac{(\partial p/\partial x)_{T,v}}{(\partial p/\partial v)_{T,x}} \quad (1.18)$$

Substituting Eqs. (1.18) into (1.5) yields

$$\left. \begin{aligned} \bar{v}_1 &= v + \frac{(\partial p / \partial x)_{T,v}}{(\partial p / \partial v)_{T,x}} x \\ \bar{v}_2 &= v - \frac{(\partial p / \partial x)_{T,v}}{(\partial p / \partial v)_{T,x}} (1-x) \end{aligned} \right\} \quad (1.19)$$

All the other partial quantities such as enthalpy, entropy, specific heat, etc., can, similarly to the partial molal fraction, be calculated from Eqs. (1.5) or (1.9). In particular, for the partial molal Gibbs energy of the constituents we have:

$$\left. \begin{aligned} \bar{g}_1 &= g(p, T, x) - (\partial g / \partial x)_{p,T} x \\ \bar{g}_2 &= g(p, T, x) + (\partial g / \partial x)_{p,T} (1-x) \end{aligned} \right\} \quad (1.20)$$

or

$$\bar{g}_1 = \left( \frac{\partial G}{\partial n_1} \right)_{p,T,n_2} \quad \bar{g}_2 = \left( \frac{\partial G}{\partial n_2} \right)_{p,T,n_1} \quad (1.21)$$

where  $g(p, T, x)$  is the molal Gibbs energy, i.e., the Gibbs energy  $G$  of a binary system, referred to one its mole by an expression similar to Eq. (1.4).

Since the derivatives in Eqs. (1.21) define chemical potentials of the constituents, it can be concluded that these potentials are identically equal to their partial molal Gibbs energies:

$$\mu_1 = \bar{g}_1 \quad \mu_2 = \bar{g}_2 \quad (1.22)$$

All the partial quantities are functions of the pressure, temperature and composition of the system and are independent of the number of moles of the constituents. Hence the partial quantities are intensive properties. Gibbs-Duhem equation (1.14) and Eq. (1.16) that follows from it is valid for any partial quantity. The molal enthalpy, entropy, specific heat and other thermodynamic properties of the moist gas can be expressed in terms of the corresponding partial quantities of the constituents employing an equation such as Eq. (1.6).

All the thermodynamic equations for pure substances and for the multicomponent system as a whole can also be applied to the system's constituents by replacing the molal quantities in these expressions by their corresponding partial molal quantities. For example, for the total Gibbs energy of a binary system we have

$$dG = -SdT + Vdp + \mu_1 dn_1 + \mu_2 dn_2 \quad (1.23)$$

whence

$$V = (\partial G / \partial p)_{T,n_1,n_2} \quad (1.24)$$

or, after dividing by the number of moles of the system  $(n_1 + n_2)$  -

$$v = (\partial g / \partial p)_{T,x} \quad (1.25)$$

We shall now differentiate Eqs. (1.20) with respect to pressure at constant temperature and water-vapor fraction of the system, while changing the order of differentiation of the second derivative. We obtain

$$\left. \begin{aligned} \left( \frac{\partial \bar{g}_1}{\partial p} \right)_{T,x} &= \left( \frac{\partial g}{\partial p} \right)_{T,x} - \left( \frac{\partial}{\partial x} \left( \frac{\partial g}{\partial p} \right)_{T,x} \right)_{p,T} x \\ \left( \frac{\partial \bar{g}_2}{\partial p} \right)_{T,x} &= \left( \frac{\partial g}{\partial p} \right)_{T,x} + \left( \frac{\partial}{\partial x} \left( \frac{\partial g}{\partial p} \right)_{T,x} \right)_{p,T} (1-x) \end{aligned} \right\} \quad (1.26)$$

whence, upon substituting Eqs. (1.25) and (1.5), we obtain

$$\bar{v}_1 = \left( \frac{\partial \bar{g}_1}{\partial p} \right)_{T,x} \quad \bar{v}_2 = \left( \frac{\partial \bar{g}_2}{\partial p} \right)_{T,x} \quad (1.27)$$

## 1.2 IDEAL-GAS SOLUTIONS

If both constituents of a gas solution mix in any ratios, such a solution is known as homogeneous. The thermodynamic properties of a binary gas solution are most conveniently calculated by integrating with respect to pressure at a given temperature from the ideal-gas state. For this reason we shall analyze in detail mixtures of ideal gases. All gases can be regarded as ideal in the case of infinitesimal pressure. A mixture of two ideal gases obeys Dalton's law

$$p = \bar{p}_1 + \bar{p}_2 \quad (1.28)$$

where

$$\left. \begin{aligned} \bar{p}_1 &= p(1-x) \\ \bar{p}_2 &= px \end{aligned} \right\} \quad (1.29)$$

are the partial pressures of the solution's constituents.

For a moist gas  $\bar{p}_1$  and  $\bar{p}_2$  are the partial pressures of the solvent gas and of the water vapor. At specified  $p$  and  $T$  the molal volumes of all the ideal gases and their mixtures are identical and equal to

$$v_{id} = RT/p \quad (1.30)$$

where  $R = 8.31441 \text{ J}/(\text{mol} \cdot \text{K})$  is the universal gas constant.

The internal energy, enthalpy, the specific heats at constant volume and at constant pressure of an ideal gas are a function of temperature only. Consequently, when ideal

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