MSE-204 Thermodynamics for Materials Science

L4. THERMODYNAMICS OF GASES

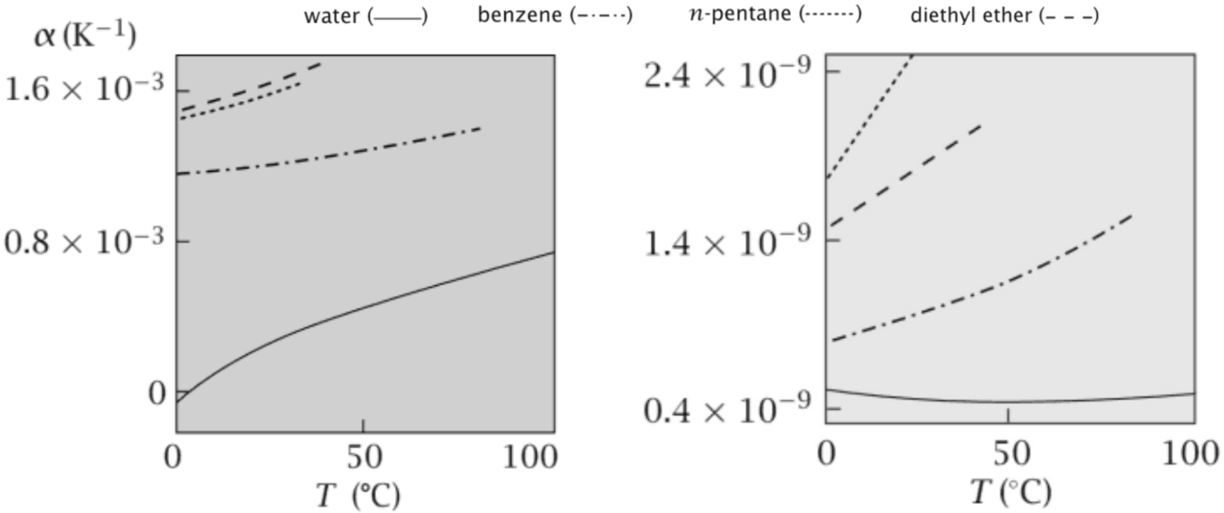
IDEAL GAS | MIXTURES OF IDEAL GASES | REAL GASES | IDEAL MIXTURES OF REAL GASES

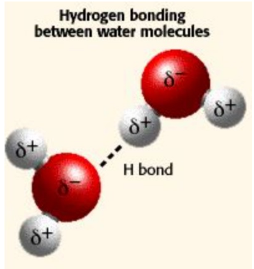
Francesco Stellacci| MXG 030

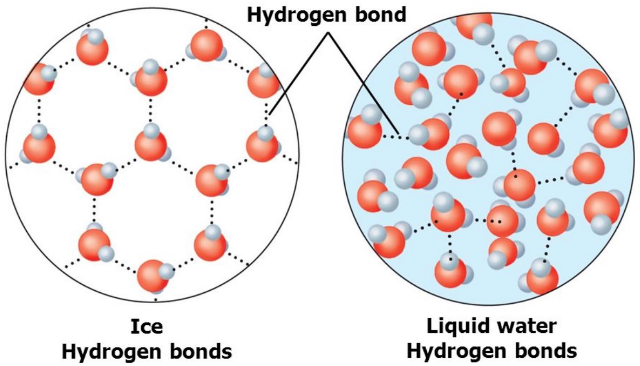
REMINDER FROM LAST WEEK

WATER DIFFERS FROM SIMPLE LIQUIDS: ENTROPY, VOLUME, & STRUCTURE

The thermal expansion coefficient and the isothermal compressibility are small for water, which is hydrogen bonded, than for simpler liquids like benzene which are not.



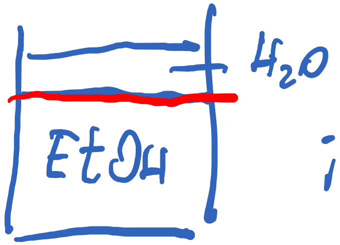




EXAMPLE | MIXTURE OF WATER & ETHANOL

Calculate the total volume before and after mixing of 1 mol of water with 100 mol of ethanol.

Data: molar volumes of pure water and ethanol are 18.00 and 58.00 cm^3/mol, respectively; the partial molar volume of water in a dilute solution of water in ethanol is 14.00 cm^3/mol.



initial

$$V_I = V_e + V_w = n_e \bar{V}_e + n_w \bar{V}_w =$$

$$100\ mol \cdot 58 \frac{cm^3}{mol} + 1\ mol \cdot 18 \frac{cm^3}{mol} =$$

$$5818\ cm^3$$

$$\bar{V}_e \simeq V_e$$

remove the menbrane

final

$$V_F = n_e \bar{V}_e + n_w \bar{V}_w = 100\ mol\ 58 \frac{cm^3}{mol} + 1 \cdot 14 \frac{cm^3}{mol}$$

$$= 5814\ cm^3$$

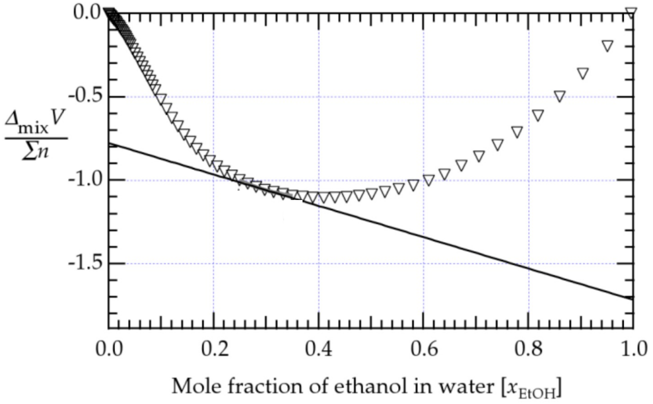
$$\Delta V^{mix} = -4\ cm^3$$

EXAMPLE | GRAPHICAL EXTRACTION OF PARTIAL MOLAR QUANTITIES

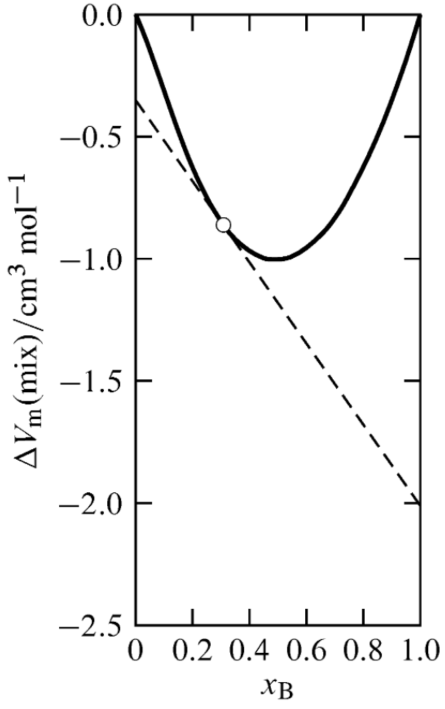
We will now determine the partial molar volumes in a water-ethanol mixture at 20°C and at a pressure of 1 atm.

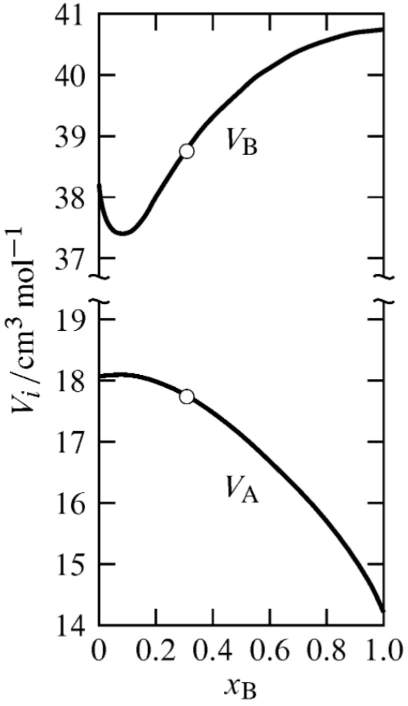
EXAMPLE | GRAPHICAL EXTRACTION OF PARTIAL MOLAR QUANTITIES

$$\frac{\Delta_{mix}V}{\sum n} = (1 - x_e)(\bar{V}_w - v_w) + x_e(\bar{V}_e - v_e)$$



EXAMPLE | GRAPHICAL EXTRACTION OF PARTIAL MOLAR QUANTITIES





EXAMPLE | ADDING SOLUTE IN DILUTE SOLUTIONS

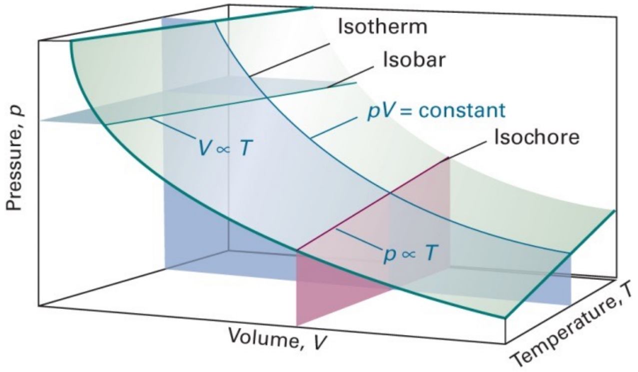
Calculate the total volume of a beaker of liquid water when it is increased by 1 mol of water, at 298 K and 1 atm.

SINGLE COMPONENT IDEAL GAS

We have introduced all of the key thermodynamics' variables. It is now time to try applying the concepts we have found to understand materials' behavior. We will start with gases as they are the simplest form of material to study in thermodynamics and slowly move to liquids and solids. The key property that renders gases easier to study is the fact that we can define an ideal state. Let's recall that an ideal gas is formed of identical molecules of negligible size in ceaseless random motion that interact only through brief elastic collisions. As a consequence, an ideal gas is a gas at 0K and infinite pressure. Obviously, this cannot be true for any material.

Yet the ideal gas law is a key stepping stone to understand the whole thermodynamics of materials. The first property of ideal gases is that they obey the ideal gas law:

$$pV = nRT$$



GIBBS FREE ENERGY AND CHEMICAL POTENTIAL OF THE IDEAL GAS

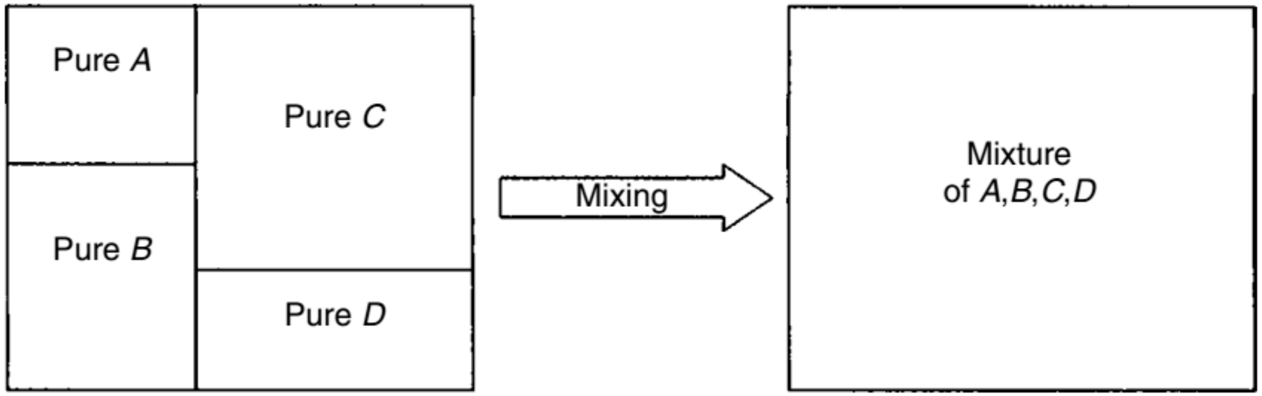
The Gibbs free energy of a single component ideal gas is:

We need now to calculate the chemical potential. To do so we will use one of Maxwell relations:

ENTHALPY AND INTERNAL ENERGY OF THE IDEAL GAS

We know that: $\left(\frac{\partial G}{\partial T}\right)_{p,n} = -S$

VOLUME AND PRESSURE IN MIXTURES OF IDEAL GASES



CHEMICAL POTENTIAL OF MIXTURES OF IDEAL GASES

The mixture of ideal gases shall have the same properties as in the case of a single gas: The mixture must consist of freely moving particles of negligible volume and the gases must exhibit negligible forces of interaction.

Similarly, to the ideal gas, we can define a gaseous mixture to be ideal if the chemical potential of each of its components is given by:

$$\mu_i = \mu_i^0(T) + RT \ln p_i \quad \text{where } p_i \equiv x_i p$$

$$\mu_i = \mu_i^0(T) + RT \ln \frac{p}{p^0} + RT \ln x_i$$

Where p is the total pressure of the gas mixture and x_i is the mole fraction of component i. Since μ_i^0 is independent of composition it retains the same value when x_i is brought to unity. It is thus precisely the same as for the ideal gas case, and it is the value of the Gibbs free energy per mole of the gas i in its pure state at unit pressure.

The concept of partial pressure makes the sum of all the partial pressures equal to the total pressure, even if the mixture is not perfect:

$$\sum_i p_i = \sum x_i p = p \sum x_i = p$$

VOLUME AND PRESSURE IN MIXTURES OF IDEAL GASES

By differentiating the chemical potential relationship at constant temperature and composition we have:

$$\left(\frac{\partial \mu_i}{\partial p}\right)_{T,n_i} = RT\frac{d\ln p}{dp} = \frac{RT}{p}$$

From Maxwell's relations we know: $\left(\frac{\partial \mu_i}{\partial p}\right)_{T,n_i} = V_i$, therefore: $V_i = \frac{RT}{p}$

The total volume of the system is: $V = \sum n_i V_i$, and therefore: $V = \frac{nRT}{p}$

The defining equation thus ensures that **the mixture will obey the gas law**.

It can be deducted that the V_i is the same for all components and is equal also to V/n. The pure gas i at the pressure p would also a molar volume, v_i, equal to RT/p. Thus:

$$V_i = V/n = v_i$$

This implies that there is **no volume change when the separate gases, each at pressure p , are put together to form a mixture** at total pressure p and at the same temperature.

It also holds that: $p_i = x_i p = x_i n\frac{RT}{V} = n_i\frac{RT}{V}$

This is known as the "law of partial pressures" or **Dalton's Law. It states that each component behaves as if no other gases were present**. According to Gibbs "It is in this sense that we should understand the law of Dalton, that every gas is as a vacuum to every other gas".

THE ENTHALPY AND INTERNAL ENERGY OF MIXING

You can intuitively calculate them by first considering the internal energy:

THE GIBBS FREE ENERGY AND ENTROPY OF MIXING

The **total Gibbs free energy of the mixture** can be written as:

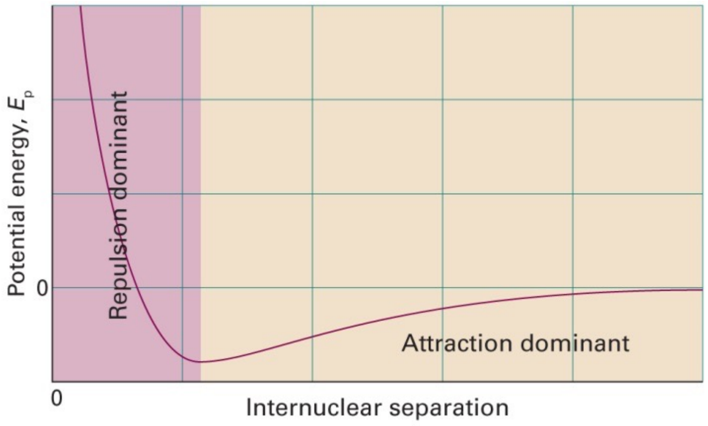
$$G = \sum n_i \, \mu_i = \sum n_i \, \mu_i^0 + RT \sum n_i \ln p_i$$

The value of G **before mixing** is obtained by summing over the various gases:

REAL GASES

We can now start studying real gases. **The molecules of these gases have interactions with each other and occupy a finite volume**. Thus, they do not follow the equation of state of the simple form.

The simplest type of interaction that we can think of is a Lennard-Jones interaction (6-12 potential):



EQUATIONS OF STATE FOR REAL GASES

Up to an atmosphere of pressure or more the behavior of most gases can be represented with fairly good accuracy by introducing into the equation of state an adjustable parameter B :

$$p(v - B) = RT$$

The quantity B has the dimensions of a volume, is usually negative at low temperatures but changes sign at high temperatures. Thus it cannot be interpreted as being proportional to the volume occupied by the molecules.

Larger deviations from the gas law can be represented by means of an equation containing a greater number of adjustable constants. A typical “two-parameter” equation is that of **van der Waals**:

$$\left(p + \frac{a}{v^2}\right)(v - b) = RT$$

Where the term $\frac{a}{v^2}$ is regarded as an “internal pressure” arising from the attractive forces between the molecules.

Large deviations from the ideal gas law can also be represented by means of the power series:

$$p = \frac{RT}{v}\left(1 + B/v + C/v^2 + \cdots\right)$$

Where $B \text{ and } C$ are called the second and third viral coefficients respectively and are in general functions of temperature. Alternatively, the volume may be expressed as a power series in the pressure.

THE FUGACITY OF A REAL GAS

We saw that the ideal gas, by definition, is one whose chemical potential, at constant temperature, is a linear function of the logarithm of its pressure.

In the case of gases which are not ideal, it is convenient to define a kind of pressure, called the fugacity, to which the chemical potential of the gas bears the same linear relationship.

Let μ be the chemical potential of the pure gas at temperature T and pressure p. The fugacity f of the gas is defined by the following relations in which **$\boldsymbol{\mu^0}$ is a function of $\boldsymbol{T}$ only**:

$$\mu = \mu^0 + RT \ln \underline{\boxed{f}} \quad \text{when} \quad \boxed{\frac{f}{p}}\boxed{\to 1} \quad \underline{\text{as} \quad p \to 0}$$

$f(T, p)$

This limiting relation makes the fugacity equal to the pressure under conditions where the gas obeys the ideal gas law.

IDEAL MIXTURES OF REAL GASES

The mixture of ideal gases has been defined as:

$$\mu_i = \mu_i^0(T) + RT\ln p + RT\ln x_i$$

where μ_i^0 is a function of temperature only. The chemical potential is thus a linear function of the logarithm of the total pressure, and this is why the mixture obeys the ideal gas law.

A much less restrictive model of a gas mixture is one that obeys the equation:

$$\mu_i = \underline{\mu_i^*(T,p)} + RT\ln x_i$$

where $\boldsymbol{\mu_i^*}$ **is both a function of temperature and pressure**. In this case, only the dependence on composition is made explicit – **the chemical potential of $\boldsymbol{i}$ depends only on its own mole fraction $\boldsymbol{x_i}$ and not on the mole fractions of any other component, at constant total pressure and temperature. This relationship defines the ideal mixture of real gases**.

THERMODYNAMIC FUNCTIONS OF IDEAL MIXTURES OF REAL GASES

Such mixtures also have **the property of having a zero volume change of mixing, zero internal energy of mixing, and a zero enthalpy of mixing at constant temperature and pressure**.

By differentiation:

$$\left(\frac{\partial \mu_i}{\partial p}\right)_T = \left(\frac{\partial \mu_i^*}{\partial p}\right)_T$$

THE FUGACITIES OF THE IDEAL MIXTURES OF REAL GASES

The definition of the ideal mixture of real gases has an important consequence to the fugacities in the mixture.
It can be shown that:

$$RT\ \ln\frac{f_i}{x_i} = \mu_i^* - \mu_i^0$$

The right-hand side is independent of composition, and therefore the ratio $\frac{f_i}{x_i}$ must remain unchanged as x_i is brought up to unity:

$$\frac{f_i}{x_i} = f_i' \quad or \quad f_i = x_i f_i'$$

where f_i' is the fugacity of pure component i at the same temperature and total pressure as the mixture. This is known as the **Lewis and Randall's rule**, i.e. **the fugacity of each constituent is equal to its mole fraction multiplied by the fugacity which it would exhibit as a pure gas, at the same temperature and the same total pressure**.

Thus, the problem of knowing the fugacity of a component of a mixture is reduced to knowing the fugacity of the same gas in its pure state.

THE ACTIVITY AND ACTIVITY COEFFICIENT OF IDEAL MIXTURES

Experimental measurements of the thermodynamic behavior of solutions are not aimed at the determination of chemical potentials, although this quantity lies at the core of the description of such systems. Common practice measures another property, the activity of component i, which is defined in terms of the chemical potential by the equation:

$$\mu_i^* - \mu_i^0 = \Delta\mu_i = RT \ln a_i$$

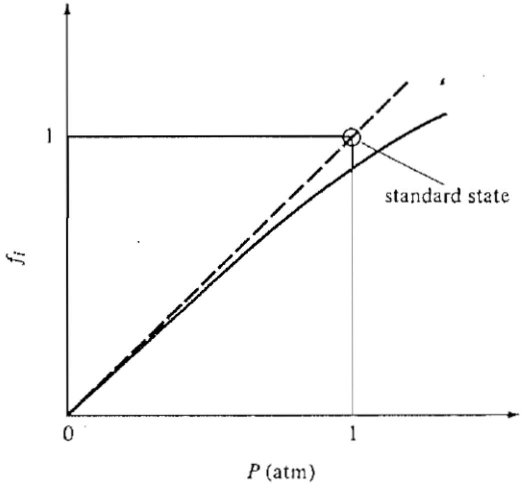
$\boldsymbol{a_i}$ **is the activity** of i in a solution **at a given temperature, pressure and composition**. **Activity is a unitless quantity**, as is the mole fraction of component i.

Another convenient measure of solution behavior, called the **activity coefficient of component i, $\boldsymbol{\gamma_i}$**, is defined as:

$$a_i = \gamma_i x_i \qquad \& \qquad \mu_i^* - \mu_i^0 = \Delta\mu_i = RT \ln \gamma_i x_i$$

If $\boldsymbol{\gamma_i = 1}$, the activity of component i is equal to its mole fraction and the behavior of i, in terms of its chemical potential is determined completely by its composition. If $\boldsymbol{\gamma_i > 1}$, $\boldsymbol{a_i > \gamma_i}$ and in the evaluation of chemical potential, component i acts as if the solution contains more i than the mole fraction suggests.

NOTE ON IDEALITY AND ITS DEVIATION [FUGACITY FUNCTION]



NOTE ON IDEALITY AND ITS DEVIATION [ACTIVITY FUNCTION]