

2106NSC

Physical & Analytical Chemistry

Thermodynamics 5

Properties of real systems

Properties of real systems

Previously we have focused on single component systems whose compositions do not change - this is clearly very restrictive.

So here, we consider multi-component systems whose compositions can vary.

When considering the free energy of real systems (as opposed to ideal systems) it is useful to introduce two new properties:

chemical potential

fugacity

Chemical potential

The value of G for one mole of ideal gas is

$$G(p) = G^\ominus + R \cdot T \cdot \ln \frac{p}{p^\ominus}$$

this can be indicated by a subscript 'm':

G_m molar Gibbs free energy
 $\mu = G_m$ **chemical potential**

$$\mu(p) = \mu^\ominus + R \cdot T \cdot \ln \frac{p}{p^\ominus}$$

The name is chosen in reminiscence of mechanical systems, where the lowest potential energy is the most stable state.

In thermodynamics, since $\Delta G < 0$ for a spontaneous process, the lowest Gibbs free energy corresponds to the most stable state.

Extensive or intensive property?

Chemical potential

The chemical potential μ equals the change of the free energy of the system, if we add $n = 1$ mol more substance.

The chemical potential μ is thus the molar Gibbs free energy of a substance, and therefore an intensive property (it is independent of the amount, since it has already been normalised against 1 mol).

Open systems and changes of composition

If we are dealing with chemical and biological systems comprising of multiple components, the composition will likely change (and some substances may leave the system we are looking at).

We thus need to consider changes in the molar amount of each substance.

So far, we have assumed that the state of a system can be expressed as a function of two variables (say T and p). However, if the composition changes, the state also depends on the amount of each substance:

$$G = G(p, T, n_1, n_2, n_i, \dots)$$

Open systems and changes of composition

To evaluate the change of the free energy of the system, we therefore need to consider the change in all properties, including the amount of each component:

$$dG = \left(\frac{\delta G}{\delta p} \right)_{T, n_i} dp + \left(\frac{\delta G}{\delta T} \right)_{p, n_i} dT + \sum_i \left(\frac{\delta G}{\delta n_i} \right)_{p, T, n_{j \neq i}} dn_i$$

From earlier considerations we know:

$$dG(p, T) = V \cdot dp - S \cdot dT$$

And we also know that the chemical potential μ is the change of the free energy of a substance when changing its molar amount ('adding 1 mol') :

$$G = n \cdot G_m = n \cdot \left(\frac{\delta G}{\delta n} \right) = n \cdot \mu$$

The fundamental equation of chemical thermodynamics

So we can substitute and obtain the fundamental equation of thermodynamics:

$$dG = V \cdot dp - S \cdot dT + \sum \mu_i \cdot dn_i$$

In chemical and biological systems (e.g. electrochemical or biological cells), T and p often remain constant, but the composition changes, and this can drive the reaction:

Extra-cellular: $c(\text{Na}^+) = 140 \text{ mM}$; $c(\text{K}^+) = 4 \text{ mM}$; $c(\text{Ca}^{2+}) = 9 \text{ mM}$

Intra-cellular: $c(\text{Na}^+) = 12 \text{ mM}$; $c(\text{K}^+) = 139 \text{ mM}$; $c(\text{Ca}^{2+}) < 0.2 \text{ }\mu\text{M}$

Fugacity: Chemical potential for real gases

In order to obtain the chemical potential

$$\mu(p) = \mu^\ominus + R \cdot T \cdot \ln \frac{p}{p^\ominus}$$

it was assumed that the gas was ideal.

Adjusting this equation for a real (non-ideal) gas, we define a new property, the **fugacity f** , which is similar to the pressure but for which

$$\mu(p) = \mu^\ominus + R \cdot T \cdot \ln(f/p^\ominus)$$

whether or not the gas is ideal.

Fugacity: Chemical potential for real gases

Expresses the tendency of the substance to escape (fugitive).

Related to how compressible the gas is, compared to the ideal gas.

Is measured in units of pressure.

The fugacity coefficient γ indicates the deviation from the ideal pressure

$$f_A = \gamma_A \cdot p_A$$

Solutions

When dealing with solutions or mixtures, the amount of a component is described in terms of

the mole fraction x_i

partial molar volume v_i

Solutions: mole fraction

The mole fraction is defined as the molar amount of an individual component divided by the total molar amount in a system:

$$x_i = \frac{n_i}{n_1 + n_2 + n_3 + \dots + n_N} = \frac{n_i}{\sum_j^N n_j}$$

It is used for gas, liquid, solid phase systems.

Solutions: partial molar volume

If two different ideal gases are combined, the total volume is the sum of the individual volumes of each gas.

However, if two different liquids are combined, the total volume is not the sum of each, due to the interactions between the liquids.

The partial molar volume of a particular substance is defined as the change in volume of a mixture, when 1 mol of the particular substance is added:

$$v_i = \left(\frac{\delta V}{\delta n_i} \right)_{p, T, n_j \neq i}$$

It is a function of the composition of the mixture to which it is added, i.e. the partial molar volume is not a constant for a given substance!

Solutions: partial molar volume

Example:

If 1 mol of water is added to a very large volume of water, the change in volume is 18 ml.

However, if 1 mol of water is added to a very large volume of ethanol (so large that each water molecule is surrounded by ethanol molecules) then the increase is just 14 ml.

The partial molar volume of water in pure water is $v(\text{H}_2\text{O}, \text{H}_2\text{O}) = 18 \text{ ml mol}^{-1}$, the partial molar volume of water in pure ethanol is $v(\text{H}_2\text{O}, \text{EtOH}) = 14 \text{ ml mol}^{-1}$.

Solutions: partial molar volume

Once determined, the partial molar volume can be used to determine the change in volume when a known amount of A is added to a solution

$$dV_{system} = v_A(x_A, x_B) \cdot dn_A + v_B(x_A, x_B) \cdot dn_B$$

and the total volume of a system of known composition is

$$V_{system} = n_A \cdot v_A(x_A, x_B) + n_B \cdot v_B(x_A, x_B)$$

Solutions: properties of a mixture

Similarly, other properties of a mixture can be expressed in terms of the molar properties and the composition:

$$G = n_A \cdot G_{m,A} + n_B \cdot G_{m,B} = n_A \cdot \mu_A + n_B \cdot \mu_B$$

Gibbs-Duhem equation

If a partial molar function (e.g. the chemical potential μ_i or the partial molar volume v_i) of one component of a mixture changes, it must be balanced by the opposing changes in the partial molar functions of the other components.

For example, water in ethanol:

$$\sum n_i \cdot dv_i = 0$$

For the chemical potential, this leads to the **Gibbs-Duhem equation**:

$$\sum n_i \cdot d\mu_i = 0$$

Suggested Reading

Hofmann, A (2016) *Introduction to Physical Chemistry*, 2nd Edition, Structural Chemistry Program, Griffith University.
Sections II.3.1-II.3.5

Atkins, PW & de Paula, J (2010) *Physical Chemistry*, 9th Edition, Oxford University Press.
Further Information 3.2 (pp. 129-130)
Sections 5.1-5.2 (pp. 156-163)