

Atmospheric Aerosols

Lecture 17

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Thermodynamics of Aerosols

Several chemical compounds (water, ammonia, nitric acid, organics, etc.) can exist in both the gas and aerosol phases in the atmosphere.

Understanding the partitioning of these species between the vapor and particulate phases requires an analysis of the thermodynamic properties of aerosols.

Since the most important "solvent" for constituents of atmospheric particles and drops is water, we will pay particular attention to the thermodynamic properties of aqueous solutions.

THERMODYNAMIC PRINCIPLES

An atmospheric air parcel can be viewed thermodynamically as a homogeneous system that may exchange energy, work, and mass with its surroundings.

Let us assume that an air parcel contains k chemical species and has a temperature T , pressure p , and volume V .

There are n_i , moles of species i in the parcel.

Internal Energy and Chemical Potential

Let us assume that the state of the air parcel changes infinitesimally (e.g., it rises slightly) but there is no mass exchange between the air parcel and its surroundings, namely, that the air parcel is a closed system.

Then, according to the first law of thermodynamics, the infinitesimal change of internal energy dU is given by

$$dU = dQ + dW$$

The infinitesimal work done on the system by its surroundings is equal to $dW = -p dV$

According to the second law of thermodynamics, the heat added to a system during a reversible process dQ_{rev} is given by

$$dQ_{\text{rev}} = T dS$$

where S is the entropy of the system.

The entropy is another property of the system (like the temperature, volume, and pressure) measuring the degree of disorder of the elements of the system; the more disorder the greater the entropy. Combining three equations:

$$dU = dQ + dW$$

$$dW = -p dV$$

$$dQ_{\text{rev}} = T dS$$

$$dU = T dS - p dV$$

According to this equation,

$$dU = T dS - p dV$$

if the number of moles of all system species n_1, n_2, \dots, n_k remains constant, the change in internal energy U of the system depends only on changes in S and V .

However, for variable composition we must have

$$U = U(S, V, n_1, n_2, \dots, n_k)$$

and thus the total differential of U is

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V} \right)_{S, n_i} dV + \sum_{i=1}^k \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j} dn_i$$

In this expression, the subscript n_i in the first two partial derivatives implies that the amounts of all species are constant during the variation in question.

On the other hand, the last partial derivative assumes that all but the i th substance are constant. Note that for a closed system $dn_i = 0$ and from last equation

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V} \right)_{S, n_i} dV \quad *$$

Comparing $dU = T dS - p dV$ and * that are both valid for a closed system, we obtain

$$T = \left(\frac{\partial U}{\partial S} \right)_{V, n_i} \quad \text{and} \quad -p = \left(\frac{\partial U}{\partial V} \right)_{S, n_i}$$

Finally, $dU = \left(\frac{\partial U}{\partial S} \right)_{V, n_i} dS + \left(\frac{\partial U}{\partial V} \right)_{S, n_i} dV + \sum_{i=1}^k \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j} dn_i$ can be rewritten as

$$dU = T dS - p dV + \sum_{i=1}^k \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j} dn_i$$

Let us define the chemical potential of species i , specifically, μ_i , as

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j}$$

so that

$$dU = T dS - p dV + \sum_{i=1}^k \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n_j} dn_i$$

can be written as

$$dU = T dS - p dV + \sum_{i=1}^k \mu_i dn_i$$

The Gibbs Free Energy, G

Calculation of changes dU of the internal energy of a system U requires the estimation of changes of its entropy S , volume V , and number of moles n_i .

For chemical applications, including atmospheric chemistry, it is inconvenient to work with entropy and volume as independent variables.

Temperature and pressure are much more useful.

The study of atmospheric processes can therefore be facilitated by introducing other thermodynamic variables in addition to the internal energy U .

One of the most useful is the Gibbs free energy G , defined as

$$G = U + pV - TS$$

Differentiating this equ.

$$dG = dU + p dV + V dp - T dS - S dT$$

and combining

$$dG = dU + p dV + V dp - T dS - S dT$$

with ,

$$dU = T dS - p dV + \sum_{i=1}^k \mu_i dn_i$$

one obtains

$$dG = -S dT + V dp + \sum_{i=1}^k \mu_i dn_i \quad *$$

Note that one can propose using (*) as an alternative definition of the chemical potential:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, p, n_j} \quad **$$

Both definitions

$$\mu_i = \left(\frac{\partial U}{\partial n_i} \right)_{S, V, n_j}$$

and (**) are equivalent.

Equation (*) is the basis for chemical thermodynamics

For a system at constant temperature ($dT = 0$) and pressure ($dp = 0$)

$$dG = \sum_{i=1}^k \mu_i dn_i \quad *$$

After the system is enlarged m times, these quantities are now mG and mn_i .

The change in Gibbs free energy of the system is

$$\Delta G = mG - G = (m - 1)G$$

and the changes in the number of moles are

$$\Delta n_i = mn_i - n_i = (m - 1)n_i$$

and as T , P , and μ_i are constant using (*)

$$\Delta G = \sum_{i=1}^k \mu_i \Delta n_i$$

or

$$G = \sum_{i=1}^k \mu_i n_i$$

Equation

$$G = \sum_{i=1}^k \mu_i n_i$$

applies in general and provides additional significance to the concept of chemical potential. The Gibbs free energy of a system containing k chemical compounds can be calculated by

$$G = \mu_1 n_1 + \mu_2 n_2 + \cdots + \mu_k n_k$$

that is, by summation of the products of the chemical potentials and the number of moles of each species. Note that for a pure substance

$$\mu_i = \frac{G}{n_i}$$

and thus the chemical potential is the value of the Gibbs free energy per mole of the substance.

One should note that both

$$dG = -S dT + V dp + \sum_{i=1}^k \mu_i dn_i \quad *$$

and

$$G = \sum_{i=1}^k \mu_i n_i \quad *$$

are applicable in general. It may appear surprising that T and p do not enter explicitly in (*). To explore this point a little further, differentiating (*)

$$dG = \sum_{i=1}^k n_i d\mu_i + \sum_{i=1}^k \mu_i dn_i$$

and combining with (*), we obtain

$$-SdT + Vdp = \sum_{i=1}^k n_i d\mu_i$$

Gibbs-Duhem equation

Conditions for Chemical Equilibrium

The second law of thermodynamics states that the entropy of a system in an adiabatic ($dQ = 0$) enclosure increases for an irreversible process and remains constant in a reversible one.

This law can be expressed as

$$dS \geq 0$$

Therefore a system will try to increase its entropy and when the entropy reaches its maximum value the system will be at equilibrium.

One can show that for a system at constant temperature and pressure the criterion corresponding to $dS \geq 0$ is

$$dG \leq 0$$

Consider the reaction $A \rightleftharpoons B$, and let us assume that initially there are n_A moles of A and n_B moles of B. The Gibbs free energy of the system is, using

$$G = \sum_{i=1}^k \mu_i n_i$$

$$G = n_A \mu_A + n_B \mu_B$$

If the system is closed

$$n_T = n_A + n_B = \text{constant}$$

Sketch of the Gibbs free energy for a closed system where the reaction $A \rightleftharpoons B$ takes places versus the mole fraction of A.

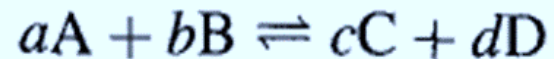
and this equation can be rewritten as

$$G = n_T(x_A\mu_A + (1 - x_A)\mu_B)$$

where

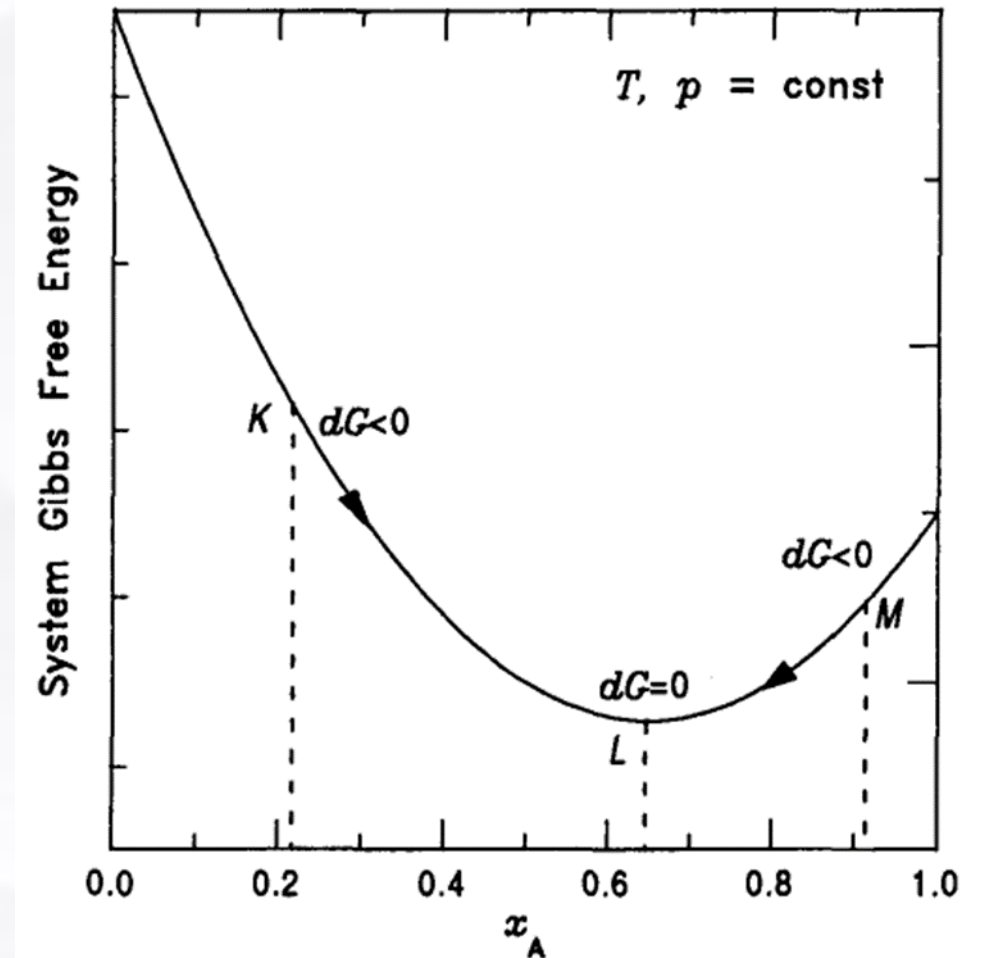
$$x_A = \frac{n_A}{n_A + n_B} = \frac{n_A}{n_T}$$

the mole fraction of A in the system. Let us assume that the Gibbs free energy of the system is that shown in Figure.



which can be rewritten mathematically as

$$aA + bB - cC - dD = 0$$



The Gibbs free energy of the system is given by

$$G = n_A\mu_A + n_B\mu_B + n_C\mu_C + n_D\mu_D$$

If dn_A moles of A react, then, according to the stoichiometry of the reaction, they will also consume $(b/a)dn_A$ moles of B and produce $(c/a)dn_A$ moles of C and $(d/a)dn_A$ moles of D.

The corresponding change of the Gibbs free energy of the system at constant T and p is, according to

$$\Delta G = \sum_{i=1}^k \mu_i \Delta n_i$$

$$\begin{aligned} dG = \mu_A dn_A + \mu_B dn_B + \mu_C dn_C + \mu_D dn_D &= \mu_A dn_A + \frac{b}{a}\mu_B dn_A - \frac{c}{a}\mu_C dn_A - \frac{d}{a}\mu_D dn_A \\ &= \left(\mu_A + \frac{b}{a}\mu_B - \frac{c}{a}\mu_C - \frac{d}{a}\mu_D \right) dn_A \end{aligned}$$

At equilibrium $dG = 0$ and therefore the condition for equilibrium is

$$\mu_A + \frac{b}{a}\mu_B - \frac{c}{a}\mu_C - \frac{d}{a}\mu_D = 0$$

or

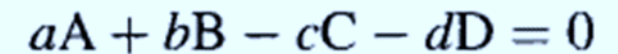
$$a\mu_A + b\mu_B - c\mu_C - d\mu_D = 0$$

Let us try to generalize our conclusions so far. The most general reaction can be written as

$$\sum_{i=1}^k v_i A_i = 0$$

where k is the number of species, A_i , participating in the reaction, and v_i the corresponding stoichiometric coefficients (positive for reactants, negative for products).

One can easily extend our arguments for the single reaction



to show that the general condition for equilibrium is

$$\sum_{i=1}^k v_i \mu_i = 0$$

This is the most general condition of equilibrium of a single reaction and is applicable whether the reactants and products are solids, liquids, or gases.

If there are multiple reactions taking place in a system with k species

$$\begin{aligned}\sum_{i=1}^k v_{i1} A_i &= 0 \\ \sum_{i=1}^k v_{i2} A_i &= 0 \\ &\vdots \\ \sum_{i=1}^k v_{in} A_i &= 0\end{aligned}$$

the equilibrium condition applies to each one of these reactions and therefore at equilibrium

$$\sum_{i=1}^k v_{ij} \mu_i = 0, \quad j = 1, \dots, n$$

where v_{ij} is the stoichiometric coefficient of species i in reaction j (there are n reactions and k species).