

UNIT THREE: MASS TRANSFER (DIFFUSION)

XVII. Fick's law of diffusion

A. introduction

I. components and phases

Some thermodynamics texts define a **phase** as "a homogeneous and uniform state of matter." A phase is bounded by an *interface* (or several interfaces), surface(s) of discontinuity in properties. Thus the liquid phase in a glass of water is bounded by the interfaces between liquid and glass and between liquid and gas (air) above. This definition has to be modified, however, when chemical diffusion occurs through a phase in response to gradients of concentration. In this case a phase is not homogeneous. Nevertheless, each phase is still bounded by interfaces, surfaces of discontinuity in properties between it and other phases. Thus the most general definition of a phase would then be

a region bounded by interfaces (discontinuities in properties) and unbroken by interfaces within

A **component** is a chemical species, such as water (H_2O), methane (CH_4), or decane ($C_{10}H_{22}$).

Sometimes for simplicity we lump many components that behave almost as one component into one "pseudocomponent," as though it were one chemical species. For instance, one might lump the thousands of petroleum chemical species into one component "oil" in an oil/water system. If water vapor (H_2O) diffuses through air, it might be convenient to lump all the non- H_2O components (N_2 , O_2 , argon, etc.) into one component, "air," in order to study the diffusion of H_2O through this gas.

Examples:

Water, ice, and water vapor are examples of phases, which might contain only one component (H_2O).

In another case, there may be other components (N_2 and O_2) along with the water vapor in the gas phase. Then the vapor phase has three or more components (N_2 , O_2 , H_2O); the liquid could have three components also if N_2 and O_2 have dissolved into the water; there might even be traces of N_2 and O_2 in the ice if ice is present.

In another case, there may be NaCl in the liquid water; there is likely to be virtually no NaCl in the vapor or the solid ice. Then there would be 4 components and 3 phases. Much of the confusion about phases and components probably reflects the fact that in English we sometimes use the same words for both components and phases: for instance, "water" the component (H_2O) and "water" the phase (liquid H_2O , possibly with some salts or gases - other components - dissolved in it).

Fick's law of diffusion in terms of mass *

$$N_A = \rho D_{AB} \nabla \omega_A \leftarrow \text{mass fraction of A}$$

mass flux of component A (kg/(m²s)) density Diffusion coefficient

3. review of concepts from thermodynamics

There are some concepts from thermodynamics that are crucial to understanding and quantifying diffusion and mass transfer. If you are unsure of any of the following concepts, you should review your notes from thermodynamics classes:

- composition
- moles
- mass fraction
- mole fraction
- concentration
- ideal gas law
- partial pressure and vapor pressure

For consistency with other S. I. units, we will work with "kgmoles" instead of "moles" (which strictly means "gram-moles"). Just as a gram mole ("gmole" or usually "mole" for short) is a mass of a material in grams equal to its molecular weight (e.g., 18 grams of H₂O = 1 gram mole of water; 32 grams of O₂ = 1 gram mole of oxygen gas), a kgmole is the mass of a material in kilograms equal to its molecular weight (18 kg H₂O or 32 kg O₂). You may have encountered the same idea in the unit "lbmole" (18 lb H₂O or 32 lb O₂) which is sometimes used in thermodynamics with English-system units. You can either think of the kgmole as the a mole in kg units, or think of it as a "kilo-mole," i.e., 1,000 gmoles of the substance.

Ironically, the S. I. system officially adopted gmoles, not kgmoles, as its units of amount of a chemical species while kg are its units of mass. I am told that the chemists were too stubborn to give up their familiar "gmole" unit! This results in factors of 1,000 being needed to keep consistent units in various formulas. To avoid this problem, in PGE 383, we work with kgmoles instead. Then the factors of 1,000 are not needed in any of the formulas.

The following are some definitions and relations important in this course:

- ρ = density = total kg / m³
- c = concentration = total kgmoles / m³
- c_A = concentration of component "A" = kgmoles component A / m³
- x_A mole fraction of component A = kgmoles component A / total kgmoles
- p_A = "partial pressure of A"

For ideal gases

$$c \equiv N/V = 1/V = p/RT$$

N = total kgmoles
 V = total volume
 V = m³/total kgmoles
 (in SI units, $R = 8314.4 \text{ J/(kgmol } ^\circ\text{K)}$)

$$c_A = c x_A$$

$$p_A = p x_A$$

In terms of moles:

$$N_A = -c D_{AB} \nabla x_A \leftarrow \text{mole fraction}$$

molar flux (kgmoles/(m²s)) total molar diffusion coefficient concentration of phase (same as above) (kg moles/m³)

For dilute solutions in incompressible liquids

$$c \equiv \rho / (\text{molecular weight of liquid solvent})$$

$$c_A = c x_A$$

* This is a simplified form of Fick's law; applies to dilute solutions; see 381 for details

If c is uniform (as in ideal gases and dilute liquid solutions)

$$c dx_A/dz = dc_A/dz$$

can write Fick's law in terms of c_A or x_A !