Textbook: J. M. Smith, H. C. Van Ness, M.M. Abbott, **Introduction to Chemical Engineering Thermodynamics,** Seventh Edition, McGraw-Hill International Editions, 2005.

Supplementary References

Stanley I. Sandler, **Chemical and Engineering Thermodynamics,** Third edition John Wiley & Sons Inc, 1998.

J. Richard Elliott, Carl T. Lira, **Introductory Chemical Engineering Thermodynamics,** 2nd edition Prentice Hall International Series in the Physical and Chemical Engineering Sciences, 1999.

CHEMICAL-REACTION EQUILIBRIA

The transformation of raw materials into products of greater value by means of chemical reaction is a major industry,

Sulfuric acid,
ammonia,
ethylene,
propylene,
phosphoric acid,
chlorine, nitric acid,
urea,
benzene,
methanol,
ethanol, and
ethylene glycol

are examples of chemicals produced

These in turn are used in the large-scale manufacture of fibers, paints, detergents, plastics, rubber, paper, fertilizers, insecticides, etc.

Clearly, the chemical engineer must be familiar with

- -chemical-reactor design
- -operation
- -process design
- -thermodynamics of reactor and or/process

The rate and the equilibrium conversion of a chemical reaction depend on:

- -temperature
- -pressure
- composition of reactants

The purpose of this Chapter is to determine the effects of temperature, pressure and initial composition (or loading) on the equilibrium conversions of chemical reactions.

The general chemical reaction written here as

$$|\nu_1|A_1 + |\nu_2|A_2 + \cdots \rightarrow |\nu_3|A_3 + |\nu_4|A_4 + \cdots$$

Where

$|\nu_i|$ **= the are stoichiometric coefficients and**
Ai = stand for chemical formulas.

vi **= stoichiometric numbers,**

the sign of stoichiometric

positive for products and negative for reactants:

Thus for the reaction

$$CH_4 + H_2O \rightarrow CO + 3H_2$$

the stoichiometric numbers are

$$\nu_{CH_4} = -1 \qquad \nu_{H_2O} = -1 \qquad \nu_{CO} = 1 \qquad \nu_{H_2} = 3$$

The stoichiometric number for any inert species is zero.

For the reaction represented by Eq. the *changes* in the numbers of moles of the species present are in direct proportion to the stoichiometric numbers.

dni

Thus for the preceding reaction,

-if 0.5 mol of CH_4 disappears by reaction,
0.5 mol of H_2O must also disappear;

Simultaneously

0.5 mol of CO and
1.5 mol of H_2 are formed. .

Applying this principle to a differential amount of reaction we can write

$$\frac{dn_2}{\nu_2} = \frac{dn_1}{\nu_1} \qquad \frac{dn_3}{\nu_3} = \frac{dn_1}{\nu_1} \qquad \text{etc.}$$

The list continues to include all species. Comparison of these equations shows that

$$\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \frac{dn_3}{\nu_3} = \frac{dn_4}{\nu_4} = \cdots$$

All terms being equal, they can he identified collectively with a single quantity representing an amount of reaction. Thus a *definition* of $d\varepsilon$ is provided by the equation

$$\boxed{\frac{dn_1}{\nu_1} = \frac{dn_2}{\nu_2} = \frac{dn_3}{\nu_3} = \frac{dn_4}{\nu_4} = \cdots \equiv d\varepsilon}$$

The general relation between a differential change dn_i in the number of moles of a reacting species and $d\varepsilon$ is therefore

$$\boxed{dn_i = \nu_i \, d\varepsilon \qquad (i = 1, 2, \ldots, N)}$$