SEPARATION THERMODYNAMICS

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Contents

Summary

In this concise article, the relevant thermodynamic functions are defined for the separation of components from their mixtures. Seawater or brine being a mixture of salts and water, the equilibrium criteria are important for consideration in the desalination operations.

1. Relevant Thermodynamic Functions

The following is the fundamental equation interrelating primary thermodynamic variables for a single-phase system from which all other equations connecting the properties of such systems are derived:

$$\mathrm{d}(nU) = T\mathrm{d}(nS) - P\mathrm{d}(nV) + \Sigma(\mu_i \mathrm{d}n_i) \qquad (1)$$

The quantity μ_i, which is the chemical potential of component *i*, plays a vital role in the thermodynamics of phase and chemical equilibria. Equation (1) suggests possible combinations of terms that may be defined as primary functions; the most important are the following.

$$\text{Internal energy:} \quad U$$

$$\text{Enthalpy:} \quad H = U + PV \tag{2}$$

$$\text{Helmholtz function:} \quad A = U - TS \tag{3}$$

$$\text{Gibbs function (also called free energy):} \quad G = U + PV - TS = H - TS \tag{4}$$

For one mole of a homogeneous fluid having a constant composition, the following relations can be written

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V \tag{5}$$

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P \tag{6}$$

$$\mathrm{d}A = -P\mathrm{d}V - S\mathrm{d}T \tag{7}$$

$$\mathrm{d}G = V\mathrm{d}P - S\mathrm{d}T \tag{8}$$

Next, fugacity is defined in direct relation to the Gibbs function; for a constant composition mixture

$$\mathrm{d}G = RT\mathrm{d}\ln f \quad (\text{constant } T, x) \tag{9}$$

$$\text{with} \quad \lim_{P \to 0} \frac{f}{P} = 1.$$

It can be shown that when the ideal gas law holds, fugacity becomes equal to pressure.

2. Partial Molar Properties

A homogeneous system may contain any number of components or chemical species. If *M* represents a molar thermodynamic property of the mixture or solution, such as *U*, *H*, *S*, etc., the total system property becomes *nM*, where

$$n = \sum_i n_i$$

are the total moles in the system. It may be expected to relate the mixture property *M* to the properties M_i of the pure chemical species making up the mixture. However, no generally valid rules are known and the connection must be established experimentally for a particular system.

The total mixture property *nM* is extensive, hence, it may be convenient to apportion this property among the mixture constituents in an appropriate way. It follows from Euler's theorem on homogeneous functions that

$$nM = \sum \left[n_i \left(\frac{\partial (nM)}{\partial n_i} \right)_{T,P,n_j} \right] \tag{10}$$

from which a partial molar property

$\bar{M}_i$, of component *i* in the solution can be defined as follows

$$\bar{M}_i = \left[\frac{\partial (nM)}{\partial n_i} \right]_{T,P,n_j} \tag{11}$$

Substituting Eq. (11) into Eq. (10),

$$nM = \Sigma (n_i \bar{M}_i) \tag{12}$$

The $\bar{M}_i$s, are homogeneous functions of zero degree in the mole numbers; therefore, they are intensive thermodynamic properties. Thus, Eq. (11) determines how the mixture property can be apportioned among the mixture constituents and Eq. (12) shows that the total mixture property is the sum of component properties. Dividing Eq. (12) by *n* converts it on a mole basis, i.e.

$$M = \sum (x_i \bar{M}_i) \tag{13}$$

where x_i represents the mole fraction of *i* in the mixture.

The equations for partial properties can be applied on a unit mass basis as well. In this case, mass *m* replaces moles *n* and x_is represent mass fraction. Furthermore, it is readily shown that

$$\bar{H}_i = \bar{U}_i + P\bar{V}_i ; \bar{A}_i = \bar{U}_i - T\bar{S}_i ; \bar{G}_i = \bar{H}_i - T\bar{S}_i .$$

Equation (12) is a general relationship for any homogeneous system in an equilibrium state. Therefore, changes in *nM* caused by changes in *P*, *T*, or the n_is are given by the total differential

$$\mathrm{d}(nM) = \left[\frac{\partial (nM)}{\partial T} \right]_{P,n} \mathrm{d}T + \left[\frac{\partial (nM)}{\partial P} \right]_{T,n} \mathrm{d}P + \sum (\bar{M}_i \, \partial n_i) \tag{14}$$

Furthermore,

$$\mathrm{d}(nM) = \sum(n_i \mathrm{d}\bar{M}_i) + \sum(\bar{M}_i \mathrm{d}n_i) \tag{15}$$

From Eqs (14) and (15),

$$n\left(\frac{\partial M}{\partial T}\right)_{P,x} \mathrm{d}T + n\left(\frac{\partial M}{\partial P}\right)_{T,x} \mathrm{d}P - \sum(n_i \mathrm{d}\bar{M}_i) = 0 \tag{16}$$

Dividing Eq. (16) by *n*,

$$\left(\frac{\partial M}{\partial T}\right)_{P,x} \mathrm{d}T + \left(\frac{\partial M}{\partial P}\right)_{T,x} \mathrm{d}P - \sum(x_i \mathrm{d}\bar{M}_i) = 0 \tag{17}$$

Equation (17) is known as the Gibbs-Duhem equation in the general form and is valid for any thermodynamic property *M* in a homogeneous phase. At constant *T* and *P*, it becomes

$$\sum(x_i \mathrm{d}\bar{M}_i) = 0 \quad (P \text{ and } T \text{ constant}) \tag{18}$$

The chemical potential μ_i is expressed as

$$\mu_i = \left[\frac{\partial(nG)}{\partial n_i}\right] \tag{19}$$

Comparing Eq. (19) with Eq. (11),

$$\mu_i = \bar{G}_i .$$

Thus, the chemical potential is identical to the partial molar Gibbs function. In the pattern of Eq. (1) for other thermodynamic properties such as the Gibbs function and substituting

$$\mu_i = \bar{G}_i$$

it can be shown that

$$-S\mathrm{d}T + V\mathrm{d}P - \sum(x_i \mathrm{d}\bar{G}_i) = 0 \tag{20}$$

Equation (20) is the most commonly encountered form of the Gibbs-Duhem equation.

2.1. Excess Properties

An excess property of solution is defined as the difference between the actual value of the property and the one that is calculated at the same condition of temperature, pressure, and composition for an ideal solution. Thus,

$$M^E = M - M_{\text{ideal}} \tag{21}$$

and

$$\Delta M^E = \Delta M - \Delta M_{\text{ideal}} \tag{22}$$

where M^E is the excess solution property and ΔM^E is the excess property change of mixing. Similarly, there are partial molar excess properties

$$\bar{M}_i^E = \bar{M}_i - \bar{M}_{i,\text{ideal}} \tag{23}$$

$$\bar{\Delta}\bar{M}_i^E = \bar{\Delta}\bar{M}_i - \bar{\Delta}\bar{M}_{i,\text{ideal}} \tag{24}$$

It can be shown that M^E and ΔM^E are identical, as are

$\bar{M}_i^E$ and $\bar{\Delta}\bar{M}_i^E$.

If M is a molar thermodynamic property of a homogeneous fluid mixture, then ΔM is defined by

$$\Delta M = M - \sum (x_i M_i^o), \tag{25}$$

where ΔM is called property change in mixing and

M_i^o

is the molar property of the pure component i at the temperature of the mixture and in some standard state of specified pressure and composition. For convenience, the standard state is chosen as that of pure i in its stable state at the mixture pressure. Substituting from Eq. (13) into Eq. (25),

$$\Delta M = \sum (x_i \bar{M}_i) - \sum (x_i M_i^o) = \sum [x_i (\bar{M}_i - M_i^o)]$$

or

$$\Delta M = \sum (x_i \bar{\Delta}\bar{M}_i), \tag{26}$$

where, by definition,

$\bar{\Delta}\bar{M}_i \equiv \bar{M}_i - M_i^o$.

For species *i* in solution, the fugacity

$$\bar{f}_i$$

is defined as

$$\mathrm{d}\bar{G}_i = RT\mathrm{d}\ln \bar{f}_i \quad (\text{constant } T), \tag{27}$$

$$\text{with } \lim_{P\to 0} \bar{f}_i/(x_i P) = 1$$

If Eq. (27) is integrated for the change of state from pure *i* in a standard state to a constituent in solution at the same *T*, then

$$\bar{G}_i - G_i^o = RT\ln\frac{\bar{f}_i}{f_i^o} \tag{28}$$

and

$$\bar{f}_{i,\text{ideal}} = x_i \ f_i^o \tag{29}$$

From the definition of

$$\overline{\Delta}\overline{M}_i$$

and Eq. (29), Eq. (28) becomes

$$\overline{\Delta}\overline{G}_{i,\text{ideal}} = RT\ln x_i \tag{30}$$

and from Eqs (26) and (30)

$$\Delta G_{\text{ideal}} = RT\sum x_i \ln x_i \tag{31}$$

and from Eqs (25) and (31)

$$G_{\text{ideal}} = \sum(x_i G_i^o) + RT\sum(x_i \ln x_i). \tag{32}$$

The most useful of these properties is the excess Gibbs function. Combining Eqs (22) and (31),

$$G^E \equiv \Delta G^E = \Delta G - \Delta G_{\text{ideal}} = \Delta G - RT\sum(x_i \ln x_i) \tag{33}$$

or

$$G^E = G - \sum (x_i G_i^o) - RT \sum (x_i \ln x_i) \tag{34}$$

Dividing Eq. (34) by *RT* puts it into a dimensionless form:

$$\frac{G^E}{(RT)} = \frac{G}{(RT)} - \sum \left[\frac{x_i G_i^o}{(RT)} \right] - \sum (x_i \ln x_i). \tag{35}$$

2.2. Activity Coefficient

An auxiliary thermodynamic function is defined as the activity coefficient for a component in the solution, as follows:

$$\gamma_i = \frac{\bar{f}_i}{(x_i f_i^o)} \tag{36}$$

where

$$f_i^o$$

is the fugacity in the standard state. Writing Eq. (36) in the following form:

$$\ln \gamma_i = \ln \left(\frac{\bar{f}_i}{f_i^o} \right) - \ln x_i \tag{37}$$

Substituting from Eqs (28) and (30),

$$\ln \gamma_i = \frac{\bar{G}_i - G_i^o}{RT} - \frac{\bar{G}_{i,\text{ideal}} - G_i^o}{RT} = \frac{\bar{G}_i - \bar{G}_{i,\text{ideal}}}{RT}$$

or

$$\ln \gamma_i = \frac{\bar{G}_i^E}{(RT)} \tag{38}$$

Equation (38) shows that ln γ_i in relation to $G^E/(RT)$ stands as a partial molar property.

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Bibliography and Suggestions for further study

Antonio Valero, (2006), THE THERMODYNAMIC PROCESS OF COST FORMATION, in Exergy, Energy System Analysis, and Optimization, [Ed. Christos A. Frangopoulos], in Encyclopedia of Life Support Systems (EOLSS), Developed under the Auspices of the UNESCO, Eolss Publishers, Oxford ,UK, [http://www.eolss.net]

Bromley L A, Singh D, Ray P A, Sridhar S and S M Read (1974) Thermodynamic properties of sea salt solution. *American Institute of Chemical Engineers (AIChE) Journal* **20**, 326-335.

C. Fritzmann, J. Lowenberg, T. Wintgens, T. Melin (2007), State-of-the-art reverse osmosis desalination," Desalination, 216 , 1-76.

Çengel, Boles - Thermodynamics, an engineering approach (5th ed) IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: http://goldbook.iupac.org (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins

Chen S F, Chan R C, Read S M and Bromley L A (1973), Viscosity of Sea water Solutions. *Desalination* 13.

J.E.Miller(2003), "Review of water resources and desalination technologies," Sandia report SAND-2003-0800,Albuquerque: Sandia National Laboratory.

Kyle B G (1984) *Chemical and Process Thermodynamics*, 2nd edn. New York: Prentice Hall International Inc.

Lewis G N and Randall M (1961) *Thermodynamics*, 2nd edn. New York: McGraw Hill Book Co.

Nafiz Kahramana, Yunus A. Cengelb, Byard Woodb and Yunus Cercic (2005),Exergy analysis of a combined RO, NF, and EDR desalination plant ,Desalination Volume 171, Issue 3,217-232

Perry R H and Green D (1984) *Perry's Chemical Engineers' Handbook*, 6th edn. New York: McGraw Hill.

R.A. Chaplin, (2006), *Power Plant Technology*, in Thermal Power Plants, [Ed. Robin A. Chaplin], in Encyclopedia of Life Support Systems (EOLSS), Developed under the Auspices of the UNESCO, Eolss Publishers, Oxford ,UK, [http://www.eolss.net]

Spiegler K S (1962) *Salt Water Purification*. New York: John Wiley.

Spiegler K S and Laird A D K (1980) *Principles of Desalination*, Parts A and B. New York: Academic Press.

Stougton R W (1965) Calculation of some thermodynamic properties of sea salt solutions at elevated temperatures from data on NaCl solutions. *Journal of Chemical Engineering Data* 10, 254.

Stougton R W (1967) Thermodynamic properties of sea salt solutions. *Journal of Chemical Engineering Data* 12, 101.

Yehia M. El-Sayed, (2003), *Cost Functions Of Components For Optimal System Design*,in Exergy, Energy System Analysis and Optimization, [Ed. Christos A. Frangopoulos], in Encyclopedia of Life Support Systems (EOLSS), Developed under the Auspices of the UNESCO, Eolss Publishers, Oxford ,UK, [http://www.eolss.net]

Yunus Cerci (2002),Exergy analysis of a reverse osmosis desalination plant in California , DesalinationVolume 142, Issue 3, 257-266

Yunus Cerci, Yunus Cengel,Byard Wood, Nafiz Kahraman,and E. Sinan Karakas(2003),*Improving The Thermodynamic And Economic Efficiencies Of Desalination Plants: Minimum Work Required For Desalination And Case Studies Of Four Working Plants*, Agreement No. 99-FC-81-0183 Desalination and Water Purification Research and DevelopmentProgram Final Report No. 78