Special Distillation Processes

Zhigang Lei, Biaohua Chen and Zhongwei Ding

V_j

L_{j+l}

S_j^v

F_j^v

E_j
Vapor
$N_{i,j}$

Liquid

Reaction

F_j^L

Q_j^v

Q_j^L

S_j^L

V_{j-l}

L_j
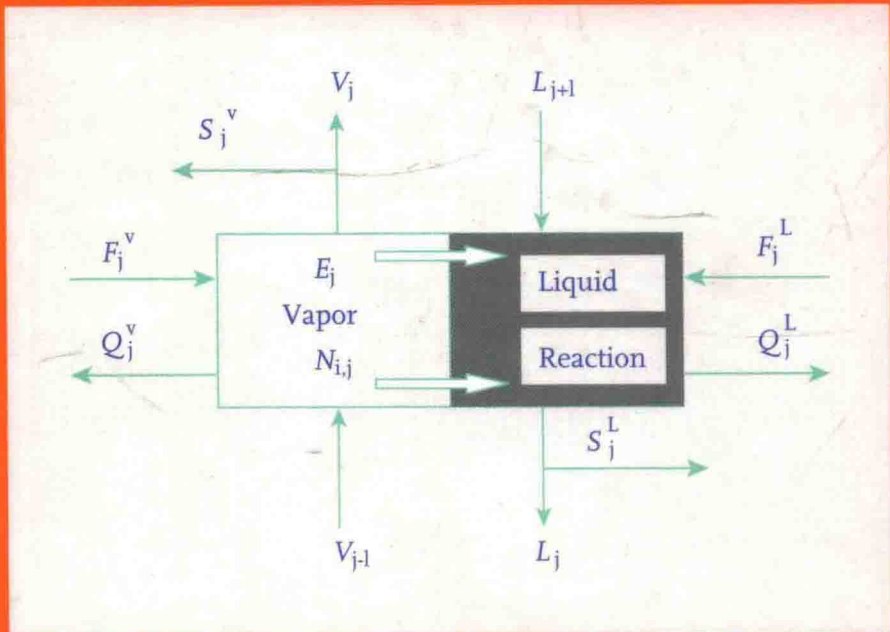
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Preface

With its unique advantages in operation and control, distillation is a very powerful separation tool in the laboratory and industry. Although many promising separation methods are constantly proposed by engineers and scientists, most of them are not able to compete with distillation on a large product scale. In this book, a new term, "special distillation processes", is proposed by the authors and is the title of this book. This term signifies the distillation processes by which mixtures with close boiling points or those forming azeotropes can be separated into their pure constituents. Among all distillation processes, special distillation processes occupy an important position.

Special distillation processes can be divided into two types: one with separating agent (i.e. the third component or solvent added; separating agent and solvent have the same meaning in some places of this book) and the other without separating agent. The former involves azeotropic distillation (liquid solvent as the separating agent), extractive distillation (liquid and/or solid solvents as the separating agent), catalytic distillation (catalyst as the separating agent by reaction to promote the separation of reactants and products), adsorption distillation (solid particle as the separating agent) and membrane distillation (membrane as the separating agent); the latter involves pressure-swing distillation and molecular distillation. However, the former is implemented more often than the latter, and thus more attention is paid to the special distillation processes with separating agent. At the same time, the techniques with a close relationship to special distillation processes are also mentioned. But it should be noted that molecular distillation is different in that its originality does not originate from the purpose of separating mixtures with close boiling points or forming azeotropes, but for separating heat-sensitive mixtures in medicine and biology. Hence, the content on molecular distillation is placed in the section of other distillation techniques and clarified only briefly.

Undoubtedly, special distillation processes are a very broad topic. We have tried to be comprehensive in our courage, but it would be nearly impossibly to cite every reference. Until now, some subjects in special distillation processes are still hot research topics. From this viewpoint, special distillation processes are always updated.

This book is intended mainly for chemical engineers, especially those engaged in the field of special distillation processes. It should be of value to university seniors or first-year graduate students in chemical engineering who have finished a standard one-year course in chemical engineering principles (or unit operation) and a half-year course in chemical engineering thermodynamics. This book will serve as teaching material for graduate students pursuing a master's or doctor's degree at Beijing University of Chemical Technology. In order to strengthen the understanding, some examples are prepared.

I hope that I have been able to communicate to the readers some of the fascination I have experienced in working on and writing about special distillation processes. In writing this book I have become aware that for me, the field of special distillation is a pleasure, as well as an important part of my profession. I shall consider it a success if a similar awareness can be awakened in those students and colleagues for whom this book is intended.

This book is the culmination of my past labors. Acknowledgements must recognize all those who helped to make the way possible:

Finally, due to authors' limitation in academic research and the English language, I believe that some deficiencies will inevitably exist in the text. If any problem or suggestion arises, please contact me.

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Contents

Chapter 1. Thermodynamic fundamentals

This chapter presents the thermodynamic fundamentals closely related with special distillation processes, which may facilitate readers to understand the separation principle discussed in the subsequent chapters. Some novel contents, which are commonly not involved in many classic thermodynamic texts, but necessary for the understanding, such as salt effect, nonequilibrium thermodynamic analysis and multi-component mass transfer, are covered. In accordance with the step-by-step rule, the section of vapor-liquid phase equilibrium is present at the beginning, and thus there is a little overlapping with common texts.

1. VAPOR-LIQUID PHASE EQUILIBRIUM

Phase equilibrium can be sorted into vapor-liquid, liquid-liquid, vapor-liquid-liquid, etc. Vapor-liquid phase equilibrium as the most applied and calculable form of phase equilibrium plays a major role in special distillation processes, particularly with respect to energy requirements, process simulation and sizing equipment. Thus, in this chapter this content is more highlighted. But, for the sake of immiscibility, sometimes the occurrence of two-liquid phase in the distillation column is inevitable. So on the foregoing basis vapor-liquid-liquid equilibrium is also briefly mentioned in this chapter. The details about how to numerically calculate the problem on vapor-liquid-liquid equilibrium are described in chapter 3 (azeotropic distillation) where vapor-liquid-liquid equilibrium is involved.

1.1. The equilibrium ratio

Equilibrium is defined as a state that will be returned to its initial state after any short, small mechanical disturbance of external conditions. According to the knowledge of physical chemistry, within any closed system where phase equilibrium exists, the total Gibbs free energy for all phases is a minimum because at this time there is no heat and mass transfer in the system. This is the starting point for studying phase equilibrium. On the other hand, from classical thermodynamics, the total Gibbs free energy and the change of Gibbs free energy in a single phase, i-component system are:

$$G = G(T, P, n_1, n_2, ..., n_i, ...) \tag{1}$$

and

$$dG = -SdT + VdP + \sum_i \mu_i dn_i \tag{2}$$

respectively, where T (temperature), P (pressure), n_1, n_2, $\cdots$, n_i (mole number of components 1, 2,...i,..., etc, respectively) are independent variants.

Thus, the change of total Gibbs free energy in a p-phase, i-component system is:

$$dG = \sum_{p}(-S^{(p)}dT + V^{(p)}dP + \sum_{i}\mu_{i}^{(p)}dn_{i}^{(p)}) \tag{3}$$

At equilibrium, at constant temperature and pressure,

$$dG = \sum_{p}(\sum_{i}\mu_{i}^{(p)}dn_{i}^{(p)}) = 0 \tag{4}$$

For each component i, the total number of moles is constant and equal to the initial before equilibrium:

$$\sum_{p}dn_{i}^{(p)} = 0 \tag{5}$$

Combined Eq. (5) with Eq. (4), it is shown to be

$$\mu_{i}^{(1)} = \mu_{i}^{(2)} = \mu_{i}^{(3)} = \bullet\bullet\bullet = \mu_{i}^{(p)} \quad \text{(equality of chemical potential)} \tag{6}$$

In addition, in terms of the phase equilibrium definition,

$$T^{(1)} = T^{(2)} = T^{(3)} = \bullet\bullet\bullet = T^{(p)} \quad \text{(thermal equilibrium)} \tag{7}$$

$$P^{(1)} = P^{(2)} = P^{(3)} = \bullet\bullet\bullet = P^{(p)} \quad \text{(mechanical equilibrium)} \tag{8}$$

Eqs. (6), (7) and (8) constitute the criteria of evaluating any phase equilibrium (including vapor-liquid phase equilibrium, of course).

In terms of the relationship of Gibbs free energy and fugacity in the multi-component mixture, it is given that

$$d\mu_{i}^{(p)} = RTd\ln\overline{f}_{i}^{(p)} \tag{9}$$

where R (8.314 J mol^{-1} K^{-1}) is universal gas constant. For a pure component, the partial fugacity, $\overline{f}_{i}^{(p)}$, becomes the pure-component fugacity $f_{i}^{(p)}$.

Another form of Eq. (9) is expressed as

$$\overline{f}_{i}^{(p)} = C\exp(\frac{\mu_{i}^{(p)}}{RT}) \tag{10}$$

where C is a temperature-dependent constant. If Eq. (10) is substituted into Eq. (6), then we obtain

$$\overline{f}_{i}^{(1)} = \overline{f}_{i}^{(2)} = \overline{f}_{i}^{(3)} = \bullet\bullet\bullet = \overline{f}_{i}^{(p)} \tag{11}$$

For vapor-liquid two phases, Eq. (11) is simplified as

$$\overline{f}_{i}^{V} = \overline{f}_{i}^{L} \tag{12}$$

which is the starting point of derivation of many commonly used equations for vapor-liquid phase equilibrium.

In this and subsequent chapters, some examples are designed and can be used as exercises for the interested readers to strengthen the understanding. But it should be noted that the solutions to these examples may be neither exclusive nor complete.

Example: Use the Eqs. (4) and (5), and deduce Eq. (6).
Solution: Eqs. (4) and (5) can be respectively rewritten as

$$\sum_i (\mu_i^{(1)} dn_i^{(1)} + \mu_i^{(2)} dn_i^{(2)} + \bullet\bullet\bullet + \mu_i^{(p)} dn_i^{(p)}) = 0 \tag{13}$$

$$dn_i^{(1)} + dn_i^{(2)} + \bullet\bullet\bullet + dn_i^{(p)} = 0 \tag{14}$$

Since the total number of component i in p phases is constant, there are p-1 independent variants among $n_i^{(1)}, n_i^{(2)}, \cdots, n_i^{(p)}$ and it is assumed that $n_i^{(2)}, n_i^{(3)} \cdots, n_i^{(p)}$ are independent variants. Therefore, Eq. (14) can be rearranged as

$$dn_i^{(1)} = -dn_i^{(2)} - dn_i^{(3)} - \bullet\bullet\bullet - dn_i^{(p)} \tag{15}$$

If Eq. (15) is incorporated into Eq. (13), then

$$dG = \sum_{N=2} \sum_i (\mu_i^{(p)} - \mu_i^{(1)}) dn_i^{(p)} = 0 \tag{16}$$

Because the term $dn_i^{(p)}$ as an independent variable in Eq. (16) can be arbitrarily given, it is reasonably presumed that $dn_i^{(p)} > 0$, which gives rise to Eq. (6).

For a vapor-liquid two-phase multi-component system, from the relationships of partial fugacity and pressure, as well as partial fugacity and activity coefficient, the following equations can be written:

$$\overline{f}_i^V = Py_i \overline{\phi}_i^V, \quad \overline{f}_i^L = Px_i \overline{\phi}_i^L \tag{17}$$

$$\overline{f}_i^V = y_i \gamma_{iV} \overline{f}_{iV}^0, \quad \overline{f}_i^L = x_i \gamma_{iL} \overline{f}_{iL}^0 \tag{18}$$

where $\overline{\phi}_i$ and γ_i are respectively fugacity and activity coefficients, and the superscript "0" stands for pure component.

At vapor-liquid two phase equilibrium, $\overline{f}_i^V = \overline{f}_i^L$, that is to say,

$$y_i \overline{\phi}_i^V = x_i \overline{\phi}_i^L \tag{19}$$

$$Py_i \overline{\phi}_i^V = x_i \gamma_{iL} f_{iL}^0 \tag{20}$$

Herein, the concept of equilibrium ratio K_i (or phase equilibrium constant) is introduced and defined as the ratio of mole fractions of a component in vapor and liquid phases. By Eqs. (19) and (20), K_i is

$$K_i = \frac{y_i}{x_i} = \frac{\overline{\phi}_i^L}{\overline{\phi}_i^V} \tag{21}$$

and

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_{iL} f_{iL}^0}{\overline{\phi}_i^V P} \tag{22}$$

where

$$\overline{\phi}_i^V = \phi(T, P, y_1, y_2, \bullet \bullet \bullet, y_{n-1}) \tag{23}$$

$$\overline{\phi}_i^L = \phi(T, P, x_1, x_2, \bullet \bullet \bullet, x_{n-1}) \tag{24}$$

$$\gamma_{iL} = \gamma(T, P, x_1, x_2, \bullet \bullet \bullet, x_{n-1}) \tag{25}$$

$$f_{iL}^0 = f(T, P) \tag{26}$$

Now we analyze the degree of freedom. For a vapor-liquid two phases N-component system, the number of total variants is $2(N-1) + 2 = 2N$, i.e. $(T, P, x_1, x_2, \bullet \bullet \bullet, x_{N-1}, y_1, y_2, \bullet \bullet \bullet, y_{N-1})$. Because $\sum_i x_i = 1$ and $\sum_i y_i = 1$, the number of degree of freedom equals $N-2+2 = N$. Thus, the number of independent variants is $2N-N = N$. In practice, there are four types of problems on vapor-liquid equilibrium:

(1) Total pressure and mole fraction in the liquid phase, i.e. $P, x_1, x_2, \bullet \bullet \bullet, x_{N-1}$, are given, and

need to solve bubble temperature and composition, i.e. $T, y_1, y_2, \bullet \bullet \bullet, y_{N-1}$.

(2) Total pressure and mole fraction in the vapor phase, i.e. $P, y_1, y_2, \bullet \bullet \bullet, y_{N-1}$, are given, and

need to solve dew temperature and composition, i.e. $T, x_1, x_2, \bullet \bullet \bullet, x_{N-1}$.

(3) Temperature and mole fraction in the liquid phase, i.e. $T, x_1, x_2, \bullet \bullet \bullet, x_{N-1}$, are given, and

need to solve bubble pressure and composition, i.e. $P, y_1, y_2, \bullet \bullet \bullet, y_{N-1}$.

(4) Temperature and mole fraction in the vapor phase, i.e. $T, y_1, y_2, \bullet \bullet \bullet, y_{N-1}$, are given, and

need to solve dew pressure and composition, i.e. $P, x_1, x_2, \bullet \bullet \bullet, x_{N-1}$.

The solutions to those problems have already been programmed in many business software programs as public subroutines in the mathematic models with respect to special distillation processes. When solving them, Eqs. (21) or (22) should be involved. However, sometimes it is more convenient to use Eq. (22) for calculating K_i because in the right side

of Eq. (21) $\overline{\phi}_i^L$ is relatively difficult to be derived. This is attributed to the difficulty of finding a reliable equation of sate to accurately describe the liquid phase behavior. In Eq. (22),

$\bar{\phi}_i^V$ is relative only with vapor phase, irrespective of liquid phase. On the contrary, γ_{iL} is relative only with liquid phase, irrespective of vapor phase. The term f_{iL}^0 depends on the system's temperature and pressure. Yet Eq. (22) isn't too straightforward in this form and should be transformed to conveniently fit available data.

From classic thermodynamics, it is known that

$$d \ln f_i = \frac{V_i}{RT} dP \tag{27}$$

Integrate the above equation from $P = P_i^s$ to $P =$ pressure of the system, and we obtain:

$$\ln \frac{f_{iL}^0}{f_{iL}^s} = \int_{P_i^s}^{P} \frac{V_{iL}}{RT} dP \tag{28}$$

Rearrange Eq. (28), and it is written that

$$f_{iL}^0 = f_{iL}^s \left[\exp \left(\int_{P_i^s}^{P} \frac{V_{iL}}{RT} dP \right) \right] = f_{iL}^s (PF)_i \tag{29}$$

where $(PF)_i$ is Poynting factor, and

$$(PF)_i = \exp \left[\int_{P_i^s}^{P} \frac{V_{iL}}{RT} dP \right] \tag{30}$$

If Eq. (29) is incorporated into Eq. (20), then

$$P y_i \bar{\phi}_i^V = x_i \gamma_{iL} f_{iL}^s (PF)_i = x_i \gamma_{iL} P_i^s \bullet \frac{f_{iL}^s}{P_i^s} (PF)_i = x_i \gamma_{iL} P_i^s \phi_i^s (PF)_i \tag{31}$$

Eq. (31) can be written in another form:

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_{iL} P_i^s \phi_i^s (PF)_i}{P \bar{\phi}_i^V} \tag{32}$$

Until now, no any assumption is made, and thus Eq. (32) is suitable for any pressure, including low pressure (< 200 kPa), middle pressure (< 200-2000 kPa) and high pressure (> 2000 kPa). However, in most cases, special distillation processes are implemented at low and middle pressures. Here only vapor-liquid equilibrium at low and middle pressures is discussed.

1.1.1. The equilibrium ratio K_i at low pressure

In this case, it is supposed that the vapor phase is ideal gas, which means $\bar{\phi}_i^V = 1$ and

$\bar{\phi}_i^s = 1$. In addition, the ratio of molar volume of component V_{iL} to RT, i.e. V_{iL}/RT, can be negligible. That is:

$$(PF)_i = \exp\left[\int_{P_i^s}^{P}\frac{V_{iL}}{RT}dP\right] = 1 \tag{33}$$

Thus,

$$Py_i = x_i\gamma_{iL}P_i^s \tag{34}$$

In terms of the definition of K_i, Eq. (34) becomes

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_{iL}P_i^s}{P} \tag{35}$$

If it goes a further step to assume that the liquid phase is in ideal solution, which means that $\gamma_{iL} = 1$, then

$$Py_i = x_iP_i^s \tag{36}$$

or

$$K_i = \frac{y_i}{x_i} = \frac{P_i^s}{P} \tag{37}$$

It should be noted that the assumption for the vapor phase is reasonable to some extent because the P-V-T behavior of most real gases at low pressure conforms to the ideal gas law. But the assumption for the liquid phase isn't accepted in some cases, except for such systems as benzene / toluene, hexane / heptane, etc., which have similar molecular sizes and chemical properties.

1.1.2. The equilibrium ratio K_i at middle pressure

If the assumption that $(PF)_i \approx 1$ at middle pressure is substituted into Eq. (31), then

$$Py_i\bar{\phi}_i^V = x_i\gamma_{iL}P_i^s\phi_i^s \tag{38}$$

That is,

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_{iL}P_i^s\phi_i^s}{P\bar{\phi}_i^V} \tag{39}$$

At not too high pressure, the assumption of ideal gas for the vapor phase is still valid. Therefore, Eq. (39) becomes

$$Py_i = x_i\gamma_{iL}P_i^s \tag{40}$$

which is consistent with Eq. (35).

In order to calculate K_i more accurately, it is better not to neglect $\overline{\phi}_i^V$ and ϕ_i^s, especially for polar gases. From classic thermodynamics we know:

$$\ln \phi_i = \int_0^P [Z_i - 1] \frac{dP}{P} \tag{41}$$

for the pure component, and

$$\ln \overline{\phi}_i^V = \int_0^P [\overline{Z}_i - 1] \frac{dP}{P} \tag{42}$$

for the multi-component mixture. There are many famous equations of state (EOS), such as van der Waals equation, R-K (Redlich and Kwong) equation, S-R-K (Soave-Redlich-Kwong) equation, P-R (Peng-Robinson) equation and their revisions, which can be used to determine the compressibility factors, Z_i and $\overline{Z}_i$. The interested readers can refer to any classic thermodynamic text [1-12]. One of equations of state is Virial equation of state, which has a sound theoretical foundation and can be derived from statistical mechanics. Herein, a two-term Virial equation of state is introduced as follows:

$$Z = 1 + \frac{BP}{RT} \tag{43}$$

where B (m^3 mol^{-1}) is the second Virial coefficient.

One advantage of two-term Virial equation of state is that it is simple and accurate to some extent. After Eq. (43) is incorporated into Eqs. (41) and (42) and integrated, we will obtain:

$$\ln \phi_i^s = \frac{B_{ii} P_i^s}{RT} \tag{44}$$

and

$$\ln \overline{\phi}_i^V = \left(2 \sum_{j=1}^{n} y_j B_{ij} - B_m \right) \frac{P}{RT} \tag{45}$$

where

$$B_m = \sum_i \sum_j y_i y_j B_{ij} \tag{46}$$

For pure-component non-polar molecules, the second Virial coefficient is commonly determined by the Tsonopoulos equation:

$$\frac{BP_c}{RT_c} = f^{(0)} + \omega f^{(1)} \tag{47}$$

where

$$f^{(0)} = 0.1445 - \frac{0.330}{T_r} - \frac{0.1385}{T_r^2} - \frac{0.0121}{T_r^3} - \frac{0.000607}{T_r^8} \tag{48}$$

$$f^{(1)} = 0.0637 + \frac{0.331}{T_r^2} - \frac{0.423}{T_r^3} - \frac{0.008}{T_r^8} \tag{49}$$

T_r is the reduced temperature ($T_r = \frac{T}{T_c}$), and ω is acentric factor.

For pure-component polar molecules, the second coefficient is commonly determined by the modified Tsonopoulos equation:

$$\frac{BP_c}{RT_c} = f^{(0)} + \omega f^{(1)} + f^{(2)} \tag{50}$$

$$f^{(2)} = \frac{a}{T_r^6} - \frac{b}{T_r^8} \tag{51}$$

$$a = -2.140 \times 10^{-4} \mu_r - 4.308 \times 10^{-21} \mu_r^8 \tag{52}$$

where

$$\mu_r = \frac{10^5 \mu_p^2 P_c}{T_c^2} \tag{53}$$

In Eq. (53), μ_p is dipole moment (debyes), P_c is critical pressure (atm), and T_c is critical temperature (K).

The constant b in Eq. (50) is zero for components exhibiting no hydrogen bonding, e.g. ketones, aldehydes, nitrides and ethers. And b usually ranges from 0.04 to 0.06 for hydrogen-bond components, e.g. alcohols, water and organic acids.

For multi-component mixtures, the most important is to derive the interaction Virials coefficient B_{ij} in order to calculate B_m. The simple way is by employing Eqs. (47) or (50).

But for this purpose, the combination rules must be devised to obtain T_{cij}, P_{cij} and ω_{ij}.

$$T_{cij} = (T_{ci} T_{cj})^{1/2} (1 - k_{ij}) \tag{54}$$

$$V_{cij} = \left(\frac{V_{ci}^{1/3} + V_{cj}^{1/3}}{2} \right)^3 \tag{55}$$

$$Z_{cij} = \frac{Z_{ci} + Z_{cj}}{2} \tag{56}$$

$$\omega_{ij} = \frac{\omega_i + \omega_j}{2} \tag{57}$$