

Modeling of Phase Equilibria in Reactive Mixtures

Sumitomo Chemical Co., Ltd.
Industrial Technology & Research Laboratory
Tetsuya SUZUTA



Most chemical processes contain at least two of the three phases of solid, liquid and gas. Therefore it is essential to fully understand phase equilibria for the logical design of processes and apparatus. The basic theory of phase equilibrium has already been established, but there are some exceptions which are not compliant with the theory. Many of those are influenced by chemical reactions within a certain phase or between different phases, so consideration of the reaction is necessary for precise reproduction of such unusual behavior. In this paper, some models for phase equilibria in reactive mixtures and several examples of their application in industrial plants are presented.

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Introduction^{1), 2)}

There are three states of matter: solid; liquid; and gas. Phase equilibrium is defined as a state in which matter and heat are balanced between at least two phases and each phase is present stably. The phase-equilibrium relationship of the temperature, pressure and the component composition is one of the important properties in chemical processes. Numerous measured data of phase equilibrium had been accumulated and released in the *DETERM* published by the DECHEMA (Deutsche Gesellschaft für Chemisches Apparatewesen, Germany)³⁾ and *Chemistry WebBook*⁴⁾ published by the NIST (the National Institute of Standards and Technology, USA). Furthermore, various models that can express the phase-equilibrium relationship of temperature, pressure and composition in a broad range have been developed based on the measured data. Additionally, computer simulations using such models are used for designing and analyzing the chemical process.

This paper introduces an example that can express actual phase equilibrium with high accuracy by modeling a system involving a chemical reaction, of which behavior cannot be expressed merely by a physical model generally used for expressing an equilibrium relationship (e.g., state equation, activity coefficient equation), taking into account the reaction concerned.

Modeling of Phase Equilibria Involving Chemical Reaction

1. Chemical Reaction in Phase Equilibria

During a chemical reaction, a substance recombines the atoms and atomic groups by itself or mutually with other substances and generates a new substance. Some chemical reactions involve the cleavage or formation of covalent bonding, and some occur due to the changes in ion bonding or hydrogen bonding. The former requires an activation energy to progress with a limited reaction rate, whereas the latter reaches chemical equilibrium (the state in which forward and reverse reactions balance each other) within a short period of time. Either reaction affects phase equilibrium. In the former case, as the composition of the phase in which a chemical reaction is occurring changes with time, the compositions of other phases change as well. However, in the latter case it will reach equilibrium in short time, whereby the composition of each phase will become constant. In the next section we will briefly introduce the basic phase equilibrium model (physical model) first, and subsequently introduce modeling of the phase equilibrium involving chemical reactions.

2. Fundamental Equations for Phase Equilibria⁵⁾

As described in standard physical chemistry textbooks, the ideal gas means the total absence of inter-

molecular force (assuming that molecules don't have any size). On the other hand, the ideal solution means that in a binary system of molecules A and B for example, A and B have the same size and the intermolecular forces between A and A, B and B, and A and B are all the same. In this case, the tendency that molecule A enters into the vapor phase (indicated by the partial pressure of A in the vapor phase) is proportional to x_A , the molar fraction of A. Particularly, it is said that when the factor of proportionality is equivalent to the vapor pressure p_A° of the pure substance A at a specific temperature, it conforms to Raoult's law. The solution in which all its compositions conform to the Raoult's law is defined as an ideal solution ($^\circ$ represents a pure substance.)

$$p_A = p_A^\circ x_A \quad (1)$$

In the ideal gas the partial pressure is the product of the total pressure p and the molar fraction in the vapor phase y_A . Consequently, the vapor-liquid equilibrium relationship of the system in which the gas phase is an ideal gas and the liquid phase is an ideal solution can be expressed through the following equation:

$$p y_A = p_A^\circ x_A \quad (2)$$

Therefore, in order to calculate the vapor-liquid equilibrium relationship of the so-called ideal system made of the ideal gas and ideal solution, the pure substance vapor pressure (the function of the temperature alone) of each component is required.

Because the intermolecular interaction acts on a real gas (molecules having considerable size) and the molecular size and intermolecular force are not consistent in a real solution, the correction from the ideal system is required. Thus the fugacity coefficient ϕ will be introduced to the vapor phase, and the activity coefficient γ will be introduced to the liquid phase to express the deviation from the ideal system. The fundamental equation of the vapor-liquid equilibrium of component i in general multicomponent systems is as follows:

$$\phi_i p y_i = \gamma_i p_i^\circ x_i \quad (3)$$

When calculating the vapor-liquid equilibrium in a real system, it also requires another process, which is to understand the fugacity coefficient and activity coefficient as functions of the temperature, pressure and com-

position. Thus far, we have introduced the fundamental equation of the vapor-liquid equilibrium relationship by order from top to bottom (i.e., from the ideal system to equation (3)). The left side and right side of equation (3) represent the fugacity of the vapor phase and that of the liquid phase, respectively. As described in standard physical chemistry textbooks, the phase-equilibrium conditions will be fulfilled when the temperature T , pressure p and chemical potential of components are the same in all phases. Equation (4) represents the relationship between the fugacity f and chemical potential μ , showing that the equal fugacity and equal chemical potential means the same.

$$[d\mu_i = RT d \ln f_i]_T \quad (4)$$

In many cases, under the low-pressure condition, the vapor phase fugacity coefficient can be considered to be 1 (the exceptional case is the main theme of this paper, and it will be discussed later). Under the high-pressure condition, the vapor-liquid equilibrium relationship will be obtained by calculating the fugacity of both vapor and liquid phases using the thermodynamic relation equation (5) (which is a state equation applicable to both vapor and liquid phases) instead of equation (3). However, we will not discuss its details here.

Up to around a moderate pressure, the vapor phase fugacity coefficient can be calculated using the thermodynamic relationship given in equation (5) as well as the virial-state equation (6) with the second virial coefficient.

$$RT \ln \phi_i = \int_V^\infty \left\{ \left(\frac{\partial p}{\partial n_i} \right)_{T,V,n_{j \neq i}} - \frac{RT}{V} \right\} dV - RT \ln Z_{\text{mix}} \quad (5)$$

$$Z_{\text{mix}} = 1 + \frac{B_{\text{mix}}}{RT} p \quad (6)$$

In these equations Z_{mix} and B_{mix} represent the compressibility factor of the mixture and the second virial coefficient, respectively.

Modeling of the activity coefficient is a main challenge in the low-pressure phase equilibrium. For a "physical model" created in consideration of intermolecular interaction, a model that can be extended to the multicomponent system using a constant for the binary system (a parameter in the activity coefficient equation obtained by correlating the vapor-liquid equilibrium relationship of the binary system) (i.e., a model by which the vapor-liquid equilibrium relationship of the binary system from the binary system data can be estimated)

is used. There is an activity coefficient model, i.e., the NRTL equation⁶⁾. This equation can be applied to the liquid-liquid equilibrium of a system that is separated into two liquid phases. This model is often built into process simulators and widely used.

3. Phase Equilibria of the System Involving Reaction^{7),8)}

(1) Fundamental Equation

It is difficult to accurately express the vapor-liquid equilibrium relationship of systems containing components that strongly associate or dissociate in the liquid phase, or those that associate in the vapor phase, merely by a physical model. In such systems the actual phase-equilibrium relationship can often be explained rationally by handling it in consideration of a new “chemical species” generated by the “chemical reaction.” This type of model, in which a new chemical species has been considered, is referred to as a “chemical model” versus a “physical model.”

The following description is also based on the concept of a binary system composed of molecules A and B. When assuming that in the system associated molecules A_iB_j ($i, j = 0, 1, 2, \dots$) composed of i of molecule A and j of molecule B exist, and the number of moles of A, B and A_iB_j in the solution are n_A , n_B and $n_{A_iB_j}$, respectively, the material-balance equation can be expressed as follows:

$$n_A = \sum_i \sum_j i n_{A_iB_j} \quad (7)$$

$$n_B = \sum_i \sum_j j n_{A_iB_j} \quad (8)$$

The chemical potential of associated molecules is represented as $\mu_{A_iB_j}$. Additionally, assuming that no association would occur in the system, the chemical potentials of a single molecule A and a single molecule B are represented as μ_{A1} and μ_{B1} , respectively. Assuming that the equilibrium shown below has been established between the single molecule and associated molecules, the balance of the chemical potential can be expressed as shown in equation (9):



The Gibbs energy change δG of the entire solution can be obtained using equations (7), (8) and (9) as follows:

$$\delta G = \sum_i \sum_j \mu_{A_iB_j} \delta n_{A_iB_j} \quad (10)$$

$$= \mu_{A1} \sum_i \sum_j i \delta n_{A_iB_j} + \mu_{B1} \sum_i \sum_j j \delta n_{A_iB_j}$$

$$= \mu_{A1} \delta n_A + \mu_{B1} \delta n_B \quad (11)$$

However, if the macroscopically viewed chemical potential of the solution is used, the Gibbs energy change will be as follows:

$$\delta G = \mu_A \delta n_A + \mu_B \delta n_B \quad (12)$$

From equations (11) and (12), the extremely important theorems independent of association pattern can be obtained as follows:

$$\mu_A = \mu_{A1} \quad (13)$$

$$\mu_B = \mu_{B1} \quad (14)$$

Additionally, this relationship can be established for dissociation as well. It can also be established in systems composed of self-association type molecule A.

What equations (13) and (14) indicate is that if the Gibbs energy of the multicomponent mixture composed of the associated molecular species $\{A_i\}$, $\{B_j\}$ and $\{A_kB_l\}$ is calculated and then the chemical potential of the monomer A_1 is extracted from the result, a macroscopic chemical potential of component A can be obtained. This means that the liquid-phase activity coefficient and vapor-phase fugacity coefficient can be obtained. When using an activity coefficient, the equation will be as follows:

$$\mu_A = \mu_A^\circ + RT \ln \gamma_A x_A \quad (15)$$

Therefore, from equations (13) through (15), the following equation can be obtained (the same can be applied to obtain the chemical potential of component B):

$$\ln \gamma_A = \frac{\mu_{A1} - \mu_A^\circ}{RT} - \ln x_A \quad (16)$$

(2) Ideal Associated Solution^{9), 10)}

The most convenient chemical model is the “ideal associated solution theory” which is that non-ideality of the liquid phase manifests only in the chemical equilibrium and the associated molecular species behave as an ideal solution. This supposition doesn’t seem very com-

pling in a system that generates numbers of the same associated molecular species.

If a virtual standard status is used, the chemical potential of component A_i can be expressed as follows:

$$\mu_{A_i} = \mu_{A_i}^* + RT \ln x_{A_i} \quad (17)$$

$$x_{A_i} = \frac{n_{A_i}}{\sum_i \sum_j i n_{A_i B_j}} \quad (18)$$

If equation (17) is applied to monomer A_1 , the equation will be as follows:

$$\mu_{A_1} = \mu_{A_1}^* + RT \ln x_{A_1} \quad (19)$$

Therefore, from equations (16) through (19), the following equation can be obtained:

$$\ln \gamma_A = \frac{\mu_{A_1}^* - \mu_{A_1}^{\circ}}{RT} + \ln \frac{x_{A_1}}{x_A} \quad (20)$$

When $x_A \rightarrow 1$, it will be $\gamma_A \rightarrow 1$. Therefore, if the molar fraction of monomer A_1 is expressed as $x_{A_1}^{\circ}$ when a pure component A alone is present, the following equation can be obtained from equation (20):

$$\ln x_{A_1}^{\circ} = \frac{-(\mu_{A_1}^* - \mu_{A_1}^{\circ})}{RT} \quad (21)$$

From equations (20) and (21), the following equation can be obtained:

$$\gamma_A = \frac{x_{A_1}}{x_{A_1}^{\circ} x_A} \quad (22)$$

Equation (22) is the fundamental equation of the ideal associated solution theory (the same can be applied for component B). Therefore, it comes to a problem to obtain $x_{A_1}^{\circ}$, x_{A_1} , $x_{B_1}^{\circ}$ and x_{B_1} from the actual association pattern and chemical equilibrium.

For example, assuming A and B have the following equilibrium relationship:



$x_{A_1}^{\circ} = x_{B_1}^{\circ} = 0$. When the chemical equilibrium constant of the molar fraction standard K is given, the following equations can be obtained:¹¹⁾

$$\gamma_A = \frac{kx_A - 2 + 2\sqrt{1 - kx_A x_B}}{kx_A^2} \quad \gamma_B = \frac{kx_B - 2 + 2\sqrt{1 - kx_A x_B}}{kx_B^2} \quad (23)$$

$$k = \frac{4K}{K+1} \quad (24)$$

Thus the vapor-liquid equilibrium relationship can be expressed using a chemical equilibrium constant.

Examples of Phase Equilibria Involving Reactions

This chapter introduces several examples for modeling of the phase equilibrium involving reactions in actual processes

1. Oligomerization in the Vapor Phase¹²⁾

One of the examples of the effect of equilibrium reaction occurred in the vapor phase without any catalyst to the phase equilibrium is oligomerization of lower-carboxylic acid as shown in **Fig. 1** or hydrogen fluoride caused by hydrogen bonding. As shown in **Table 1**¹³⁾, the lower-carboxylic acid with the carbon number three or less tends to form dimers in vapor phase. The consideration of this chemical equilibrium is essential to accurately calculate the vapor-liquid equilibrium relationship and the vapor-phase enthalpy. The following two methods are able to handle such systems: the ‘‘Chemical Approach’’¹⁴⁾ based on the ideal association theory; and the ‘‘Physical Approach’’^{15), 16)} in which the liquid-phase is treated with a physical model and the effect of the association in the vapor phase is reflected to the second virial coefficient of equation (6). Overviews of the both methods are shown in **Table 2**.¹⁷⁾ Additionally, in a system containing multiple lower-carboxylic acids, it is necessary to consider the association

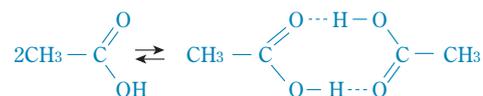


Fig. 1 Example of dimerization due to hydrogen bond (acetic acid)

Table 1 Dimerization ratio of various substances in vapor phase (100°C)

Substance	Ratio of dimer
formic acid	0.63
acetic acid	0.88
propionic acid	0.64
butylic acid	0.51
acrylic acid	0.60
acetone	0.15 – 0.22
methanol	0.11 – 0.19
ethanol	0.09 – 0.13
acetaldehyde	0.09 – 0.14
water	0.01 – 0.04

Table 2 Approach to vapor-liquid equilibrium with association in vapor phase

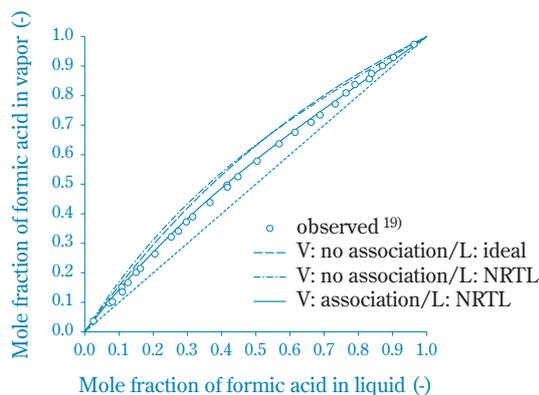
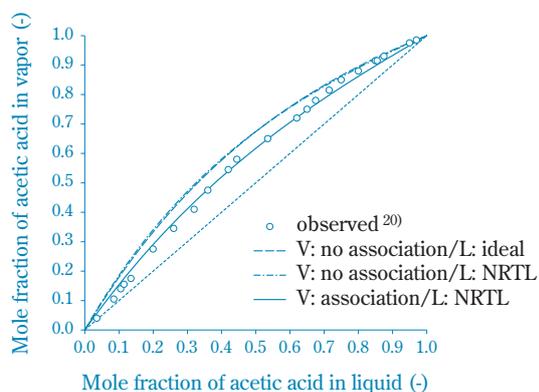
phase	“Chemical” Approach	“Physical” Approach
Vapor	Ideal Mixture of Associated Molecules	Using 2nd Virial Coeff. Correction in Equation of State
Liquid		Local Composition

[Models in Physical Approach]

Vapor Phase: Equation of State^{15),16)}Liquid Phase: Activity Coefficient Model⁶⁾

that occurs between the same type of molecules as well as that occurs between different types of molecules.

Fig. 2 compares the results obtained when the vapor-liquid equilibrium data of formic acid + acetic acid measured at 1 atm was correlated considering the association in the vapor phase to that obtained when the aforementioned data was correlated without considering any association in the vapor phase. Similarly, **Fig. 3** compares the results of the same two cases except that the system consists of acetic acid + propionic acid.

**Fig. 2** VLE of formic acid + acetic acid (1atm)
VLE: Vapor-Liquid Equilibrium
Created using data from cited reference 19).**Fig. 3** VLE of acetic acid + propionic acid (1atm)
Created using data from cited reference 20).

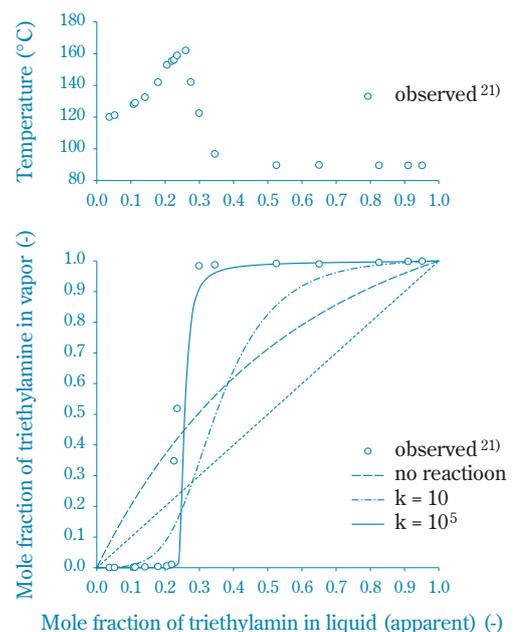
The effect of the association in the vapor phase is considered based on the Physical Approach in these correlations, and nearly the same result can be obtained through the Chemical Approach as well. Conversely, when considering the less-than-ideal character of the liquid phase's physical term alone without considering the association in the vapor phase, a divergence from the measured value can be seen. This reveals the fact that it is crucial to introduce a model that expresses the association in the vapor phase when reproducing the actual phenomenon.

2. Reaction Derived from Hydrogen Bonding in Liquid Phase

The density of the liquid phase is higher than that of the vapor phase and thus the intermolecular interaction may manifest particularly due to the hydrogen bonding. In a system that cannot be correlated with a physical model, stronger bonding and an advanced reaction other than reactions described in Section 1 may be occurring in the liquid phase. As an example of this phenomenon, this section presents the vapor-liquid equilibrium of a triethylamine + acetic acid system and a formaldehyde + methanol + water system as well as their expression models.

(1) Triethylamine + Acetic Acid System

Regarding the isobaric vapor-liquid equilibrium of this system under 1 atm, as shown in **Fig. 4**, the boiling point

**Fig. 4** VLE of triethylamine + acetic acid (1atm)
Created using data from cited reference 21).

reaches its maximum (162°C) at approximately 0.25 of the liquid-phase molar fraction of triethylamine. When more triethylamines are added, the boiling point will rapidly decrease toward 89°C, which is the normal boiling point of a pure substance.^{21), 22)} From this behavior it can be surmised that three molecules of acetic acid coordinate to one molecule of triethylamine in the liquid phase. Thus the following assumption is made based on the ideal associated solution theory:

- (i) In the liquid phase triethylamine and acetic acid molecules are bonded at the ratio of 1 : 3, forming adducts. Additionally, the chemical equilibrium is present between monomers as shown below. The equilibrium constant can be defined as shown in equation (25).

$$K = \frac{\eta_3}{\eta_1\eta_2^3} \quad (25)$$

K : Chemical equilibrium constant (molar fraction standard)

η_i : True molar fraction of component i in the liquid phase

1: trimethylamine 2: acetic acid 3: Adduct

- (ii) The liquid phase is a ternary ideal solution of monomers and adducts.
 (iii) The vapor pressure of adducts is small and can therefore be ignored.

Fig. 4 also indicates the calculation results of the vapor-liquid equilibrium relationship. Increasing the equilibrium constant to around 10^5 enabled us to make the composition closer to the measured value. Meanwhile, a spectroscopic analysis has revealed that this system has a complex structure in which an acetic acid dimer has locally coordinated to an adduct at the ratio of 1 : 1 in the liquid phase²³⁾ and that, once the apparent molar fraction of triethylamine in the liquid exceeds 0.6 in measurement, the triethylamine rich layer will separate from the adduct-rich layer and thereby cause a liquid-liquid phase separation.²⁴⁾ Although the phenomena that occur in the liquid phase has been proved to be more complex than our initial assumption, it is interesting that by taking a simple chemical equilibrium into account, the tendency of the measured data can be expressed quite accurately.

(2) Formaldehyde + Methanol + Water System

The mixture of these three components appears in a reaction product of the formaldehyde manufacturing

process by the air oxidization of methanol. If the mixture is distilled, methanol can be obtained from the column overhead and formaldehyde + water can be obtained from the column bottom.²⁵⁾ Because formaldehyde is a volatile matter having the normal boiling point of -19°C , it can be surmised that a reaction has occurred between formaldehyde and methanol or water in this distillation process.

Based on the research of the past, it is known that in this system dehydration condensation of the formaldehyde hydrate and methanol removal condensation of formaldehyde + methanol adduct (which are shown in **Table 3**) reversibly occur in the liquid phase.²⁶⁾

Considering the chemical equilibrium shown in **Table 3**, Maurer attempted to correlate the vapor-liquid equilibrium data of the formaldehyde + water system and the formaldehyde + methanol system in the liquid phase.²⁷⁾

Table 3 Chemical equilibrium in liquid phase of formaldehyde + methanol + water system
 Created using data from cited reference 28)–30).

Condensation of methylene glycol in water	
1) $\text{CH}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2(\text{OH})_2$	$\ln K = -308.51 + 20774.24/T + 43.11\ln T$
2) $2\text{CH}_2(\text{OH})_2 \rightleftharpoons \text{HO}(\text{CH}_2\text{O})_2\text{H} + \text{H}_2\text{O}$	$\ln K = 151.92 - 8666.6/T - 21.5\ln T$
3) $\text{HO}(\text{CH}_2\text{O})_2\text{H} + \text{CH}_2(\text{OH})_2 \rightleftharpoons \text{HO}(\text{CH}_2\text{O})_3\text{H} + \text{H}_2\text{O}$	$\ln K = 152.41 - 8523.3/T - 21.7\ln T$
4) $\text{HO}(\text{CH}_2\text{O})_3\text{H} + \text{CH}_2(\text{OH})_2 \rightleftharpoons \text{HO}(\text{CH}_2\text{O})_4\text{H} + \text{H}_2\text{O}$	$\ln K = 152.37 - 8502.6/T - 21.7\ln T$
5) $\text{HO}(\text{CH}_2\text{O})_4\text{H} + \text{CH}_2(\text{OH})_2 \rightleftharpoons \text{HO}(\text{CH}_2\text{O})_5\text{H} + \text{H}_2\text{O}$	$\ln K = 152.37 - 8491.2/T - 21.7\ln T$
Condensation of hemi-formal in water	
1) $\text{CH}_4\text{O} + \text{CH}_2\text{O} \rightleftharpoons \text{CH}_3\text{OCH}_2\text{OH}$	$\ln K = 95.63 - 892.7/T - 14.89\ln T$
2) $2\text{CH}_3\text{OCH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{O}(\text{CH}_2\text{O})_2\text{H} + \text{CH}_3\text{OH}$	$\ln K = -2.097 - 49.2/T$
3) $\text{CH}_3\text{O}(\text{CH}_2\text{O})_2\text{H} + \text{CH}_3\text{OCH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{O}(\text{CH}_2\text{O})_3\text{H} + \text{CH}_3\text{OH}$	$\ln K = -1.635 - 53.0/T$
4) $\text{CH}_3\text{O}(\text{CH}_2\text{O})_3\text{H} + \text{CH}_3\text{OCH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{O}(\text{CH}_2\text{O})_4\text{H} + \text{CH}_3\text{OH}$	$\ln K = -1.682 - 53.0/T$
5) $\text{CH}_3\text{O}(\text{CH}_2\text{O})_4\text{H} + \text{CH}_3\text{OCH}_2\text{OH} \rightleftharpoons \text{CH}_3\text{O}(\text{CH}_2\text{O})_5\text{H} + \text{CH}_3\text{OH}$	$\ln K = -1.709 - 53.0/T$

Based on the model shown in **Fig. 5** created using Maurer's document as a reference, **Fig. 6** and **Fig. 7** show the results of correlation of the isobaric vapor-liquid equilibrium data of each system measured at 1 atm. In either system the measured data is satisfactorily reproduced. Furthermore, this model was incorporated into a process simulator and the calculation on the dis-

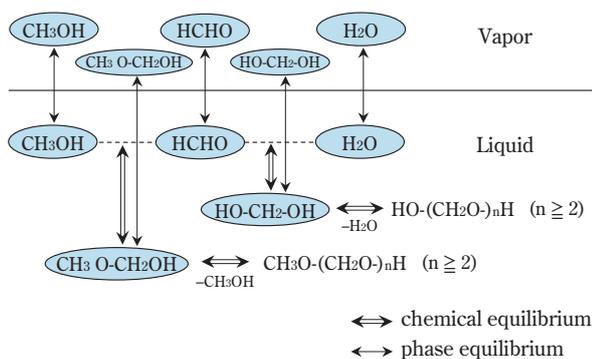


Fig. 5 Scheme of VLE for HCHO + CH₃OH + H₂O system

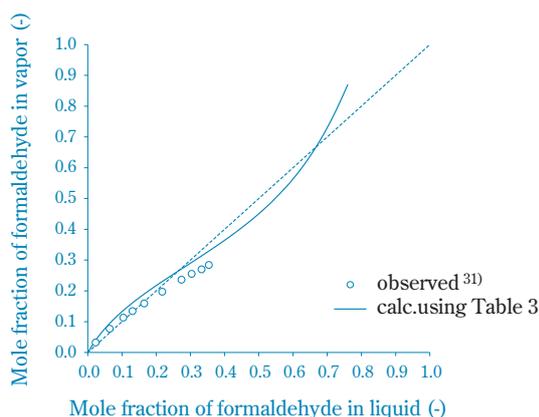
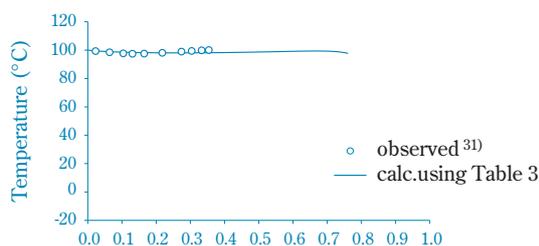


Fig. 6 VLE of formaldehyde + water (1atm)
Created using data from cited reference 31).

tillation column (in which these three components were actually separated) was performed. As a result, the plant behavior was reproduced successfully.

3. Dissociative Reaction in Liquid Phase^{33), 34)}

One of the typical reactions that occur quickly in the liquid phase is a dissociation of strong electrolytes into ions in water. HCl is a volatile component with a normal boiling point of -85°C as a pure substance. However, if HCl is diffused in $1,000\text{ cm}^3$ of water while keeping the temperature at 25°C by removing heat of dissolution under the atmospheric pressure, approximately 20 mol will be dissolved.³⁵⁾ This phenomenon results from HCl dissociation into H_3O^+ Cl^- in water as shown in **Fig. 8**, and subsequent the small percentage of molecular HCl

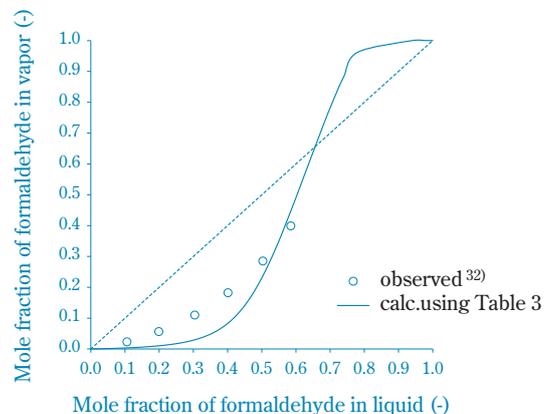
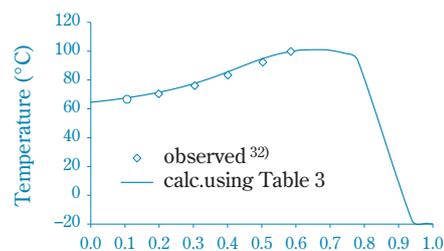


Fig. 7 VLE of formaldehyde + methanol (1atm)
Created using data from cited reference 32).

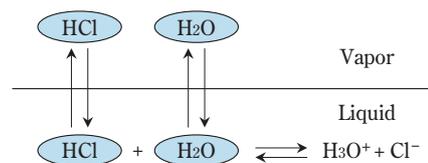


Fig. 8 Regime of VLE for HCl + H₂O system

in the liquid. As with H₂O, approximately 35% of molecules bond with H⁺ and become H₃O⁺. Moreover, because H₂O molecules are also drawn to Cl⁻ via hydrogen that have been positively charged in the molecules, the percentage of molecules that can be freely go back and forth between the liquid and the vapor phase will decrease. (Although this phenomenon is not including in **Fig. 8**.)

Typical process simulators such as Aspen Plus^{®36)} are equipped with a model containing the parameters that expresses interaction between molecules and ions and that between different kind of ions.^{37), 38)} If the model is carefully used, the impact of the major electrolyte's dissociation to the phase equilibrium can be accurately reproduced. **Fig. 9** (a) and (b) show the isobaric vapor-liquid equilibrium of HCl + H₂O system.³⁹⁾ In this system the azeotropic point where the HCl concentration becomes equal in the liquid phase (including the portion that dissociated into ions) and the vapor phase. Under the constant pressure, the temperature

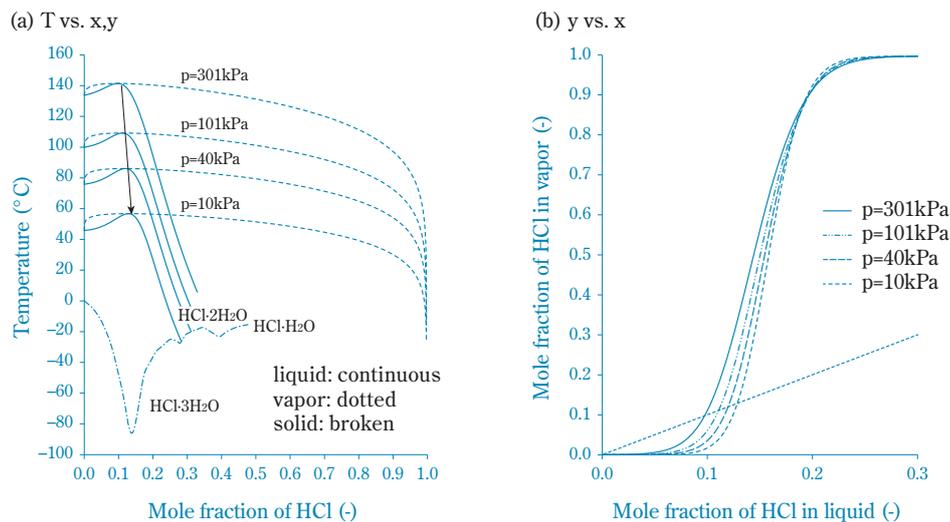


Fig. 9 Isobaric VLE of HCl + H₂O system
Created using data from cited reference 39).

reaches to its maximum in this composition. If the HCl concentration further increases, the number of HCl molecules that haven't dissociated will also increase in the liquid, thus decreasing the boiling point rapidly. Furthermore, the HCl concentration at the azeotropic point depends on the pressure. The lower the pressure (is), the larger this concentration becomes. Utilizing this phenomenon, HCl and H₂O can be finely separated.⁴⁰⁾ For example, when hydrochloric acid composed of 10 mol% of HCl and 90 mol % of H₂O is distilled in a column, in which the pressure has been reduced to 10 kPa, as shown in **Fig. 10**, H₂O is discharged from the column overhead, and from the column bottom, liquid having a composition similar to the azeotropic composition at this pressure (HCl 12 mol%) can be obtained. Next, the bottom liquid is fed to a column that has been pressurized to 300 kPa. HCl concentrated vapor will be stripped from the column overhead. From the column bottom, the liquid of near azeotropic composition at this pressure (HCl 9 mol%) will be obtained. If the vapor from the column overhead is cooled down to near normal temperature, the gas will become nearly 100% of HCl. The condensed liquid while cooling can be recycled back to the column. Furthermore, if the bottom liquid and raw materials are fed to the previous column at reduced pressure, the entire HCl in the feed liquid will be separated from H₂O and can be obtained from the pressured column. Thus HCl and H₂O—which cannot be completely separated merely by using a single column—can be separated almost completely using two columns at different pressures.^{41)–43)}

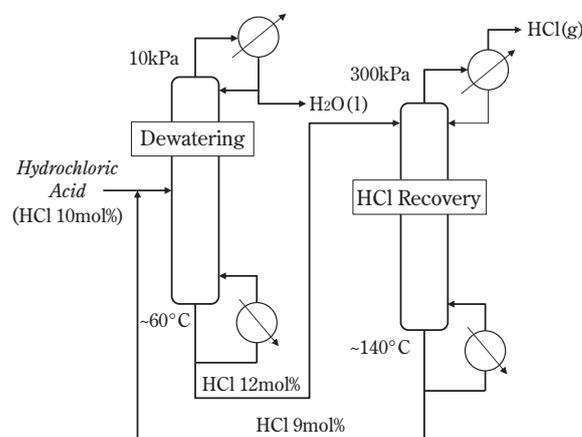


Fig. 10 HCl-H₂O separation with two columns under different pressure

4. Reaction Between Heterogeneous Phases

Till this point, we have described the effects of reactions (–) which occur either in the vapor phase or the liquid phase (–) to the phase equilibrium. However, in some cases a reaction between heterogeneous phases dominates the phase equilibrium. An example of such a case is shown below.

If the aqueous solution into which chlorine gas has been kept blowing is cooled below 10°C, light-yellow crystals start to precipitate at a certain time.⁴⁴⁾ They are chlorine hexahydrates and have a chemical equilibrium relationship with hydrogen and water in the vapor phase. When the right side of the following equation, which is the product of the partial pressures of the aforementioned matters, exceeds the equilibrium constant K_p , the deposition occurs.

$$K_p = p_{\text{Cl}_2} p_{\text{H}_2\text{O}}^6 \quad (26)$$

K_p is a function of the temperature alone. According to the literature data⁴⁰⁾ and our experiment, when [atm] is used as a unit of partial pressure, the temperature dependency (unit [K]) can be expressed as follows:⁴⁵⁾

$$\ln K_p = 118.56 - 41065/T \quad (27)$$

Fig. 11 depicts the relationship between temperature and the dissociation pressure of the hydrate ($= p_{\text{Cl}_2} + p_{\text{H}_2\text{O}}$). If ions in the liquid are present around the positive anode in an electrolytic cell, H₂O molecules are drawn to them and the dissociation pressure will decrease in the vapor phase. Because dissociation equilibrium strongly depends on the dissociation pressure of water, hydrates are not easily generated in this type of liquid. If the temperature decreases in gas piping or the like, crystals will deposit directly from the vapor phase, and this may cause some troubles such as pipe clogging. It is therefore necessary to take precautions.

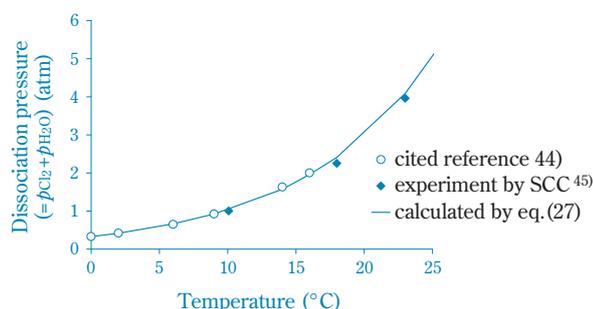


Fig. 11 Dissociation of pressure of $\text{Cl}_2 \cdot 6\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{Cl}_2(\text{g}) + \text{H}_2\text{O}(\text{g})$
Created using data from cited reference 44), 45).

Conclusion

Reactions are often involved in peculiar phase-equilibrium relationships. Particularly, a system having the maximum boiling point at the constant pressure, or a system having the minimum vapor pressure at the constant temperature along the composition in its vapor-liquid equilibrium is assumed to involve a chemical reaction in the liquid phase. In such a case, the actual behavior may be reproduced by extracting the true chemical species that are present in the liquid phase and giving a reasonable chemical equilibrium that determines their presence ratio. However, confirming

the presence of a chemical equilibrium through analysis is not necessarily easy because its status can quickly change during sampling. It can therefore be assumed that it is valid to estimate a chemical equilibrium using free energy.⁴⁶⁾ Information on the standard free energy of formation ΔG_f° of numerous substances including solid matters have also been accumulated in the thermodynamics databases of the DECHEMA and NIST.^{2), 3)} Additionally, simulators using such information have been developed to perform equilibrium computation and create a phase diagram. Furthermore, in the scientific field, equilibrium estimation is performed using a quantum chemical calculation, and reaction paths and products are estimated using an artificial intelligence.⁴⁷⁾ We hope to precisely understand and appropriately handle the presence of reactions that affect an important phase equilibrium by fully utilizing such information and new methods, and consequently establish a more reliable process.

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PROFILE



Tetsuya SUZUTA

Sumitomo Chemical Co., Ltd.
Industrial Technology & Research Laboratory
Senior Research Specialist