

# A THERMODYNAMIC ANALYSIS OF HEAT INTEGRATION IN CRYOGENIC SEPARATION PROCESS SYSTEMS

KAZUO NIIDA, KATSUO SHIROKO AND TOMIO UMEDA

Chiyoda Chemical Engineering and Construction Co., Ltd.,  
P. O. Box 10, Tsurumi, Yokohama 230

**Key Words:** Distillation, Separation Process, Cryogenic System, Available Energy, Heat Availability Diagram, Thermodynamic Analysis, Heat Recovery

Presented is a method for fundamental analyses and heat integration of process systems at cryogenic temperature by using a heat availability diagram which is constructed by plotting a temperature function  $(1 - T_0/T)$  against heat load  $Q$ , based on available energy concept of thermodynamics. The function takes values between unity and minus infinity. By using the diagram, heat availability and available energy loss in a process system at cryogenic temperature are thoroughly analyzed, and the maximum theoretical rate of heat recovery is determined. A series of bottlenecks in heat recovery are sequentially found, and modified heat recovery systems are evolved.

## Introduction

The need for energy conservation has been widely recognized, and various methods for efficient use of energy have been applied in particular to chemical processes which are essentially energy-intensive systems. It is important to establish a systematic method of reducing external energy inputs by effective utilization of heat in chemical processes. The authors' group has recently developed a practical approach to process analysis and improvements in energy conservation by using a heat availability diagram based on the available energy concept of thermodynamics. This approach has been applied to process systems involving units and streams whose temperatures are higher than ambient temperature, i.e., distillation systems,<sup>1,6,8)</sup> chemical process systems,<sup>6,7)</sup> and steam-power systems.<sup>5)</sup>

This paper attempts to extend the approach to the effective use of heat in process systems dealing with cryogenic temperatures, such as ammonia processes, ethylene processes, power generation systems from LNG cold, and so on. This paper consists of the following three parts. Firstly, the concept of available energy and the heat availability diagram are described in order to clarify the characteristics of cold energy. Secondly, a binary distillation system operating at cryogenic temperatures is analyzed to grasp the thermodynamic characteristics of the system. Finally, a method of synthesizing heat integration systems so as to minimize the losses of available energy in process systems is presented.

## 1. Available Energy and Heat Availability Diagram

The necessity of thermodynamic analysis of a process system, long recognized, has recently received renewed attention. In addition to system analysis using the First Law of Thermodynamics, analysis by the Second Law of Thermodynamics has been carried out to evaluate energy quality. Among several ways of applying the Second Law, the practical usefulness of the available energy concept has been recognized. The available energy of a system is defined as the maximum useful work which could be obtained by bringing the system to its dead-state, which is in equilibrium with the environment.<sup>3)</sup>

In a steady-state flow system, the available energy of a mixture, where such factors as kinetic and potential energies are neglected, is defined as follows:

$$A = \int_{\text{dead-state}}^{\text{state}} dA = \int_{\text{dead-state}}^{\text{state}} (dH - T_0 dS) \quad (1)$$

where the dead-state is the state of zero available energy. Enthalpy,  $H$ , and entropy,  $S$ , of the mixture can be respectively defined as follows:

$$dH = T dS + V dP + \sum_i \mu_i dn_i \quad (2)$$

$$dS = dQ/T \quad (3)$$

Substituting Eqs. (2) and (3) into Eq. (1) gives

$$A = \int_{\text{dead-state}}^{\text{state}} \left\{ (1 - T_0/T) dQ + V dP + \sum_i \mu_i dn_i \right\} \quad (4)$$

The following integration path can be taken:

Received April 20, 1983. Correspondence concerning this article should be addressed to K. Niida.

$$A = \int_{\text{pseudo-dead-state}}^{\text{state}} \{(1 - T_0/T)dQ + VdP\} + \int_{\text{dead-state}}^{\text{pseudo-dead-state}} \left\{ VdP + \sum_i \mu_i dn_i \right\} \quad (5)$$

where the pseudo-dead-state is a state whose temperature and pressure are equal to those of the dead-state. The first and second integrals are called physical and chemical available energy, respectively. Chemical available energy of a pure component can be calculated by using a table of standard available energy at the temperature of the dead-state as a reference temperature.<sup>2)</sup> The first term in the first integral of Eq. (5) is called the thermal available energy. A change of the thermal available energy of the mixture from a state 1 to another 2 can be expressed as follows.

$$\Delta A_{\text{thermal}} = \int_{\text{state 1}}^{\text{state 2}} (1 - T_0/T)dQ \quad (6)$$

The above equations obviously have no restriction against application to systems with cryogenic temperatures.

It is possible to make a graphical representation of thermal available energy by plotting a temperature function,  $(1 - T_0/T)$ , against heat flow,  $Q$ , as shown in **Fig. 1**. This is called a heat availability diagram. The temperature function takes values between unity and minus infinity and has a negative value when a temperature  $T$  is below the ambient temperature  $T_0$ . The temperature function corresponds to the Carnot efficiency when a temperature is above ambient temperature.<sup>1,6)</sup> The dotted line in the diagram, called the dead-state line, is associated with the zero value of the temperature function. If a heat availability line for a mixture is plotted on the diagram from the ambient temperature to another temperature under a constant pressure, the thermal available energy for the mixture is expressed by the area enclosed between that line and the dead-state line. On the diagram shown in **Fig. 1(a)**, the slashed area under the line from state 1 to state 2 corresponds to the decrease in available energy for a heat source stream with temperature higher than ambient temperature. The other slashed area on the diagram, above the line from state 3 to state 4, corresponds to the increase in available energy for the heat source stream with temperatures lower than ambient temperature. Similarly, for the heat sink stream shown in **Fig. 1(b)**, there exists the same relationship between slashed area and available energy change for the mixture as summarized in the description of **Fig. 1(a)**. It is worthwhile to recognize that the change of thermal available energy with respect to a temperature change of the stream in the lower-temperature region is larger than that in the higher-temperature region, as can be seen in **Fig. 1**.

## 2. Process Analysis

There is no loss of available energy in a system which is reversible and ideal. Since every real system is irreversible, there exist losses of available energy in the system. Consequently, it is important to bring a real system closer to a reversible one by reducing losses of available energy in the system. The cryogenic binary distillation system shown in **Fig. 2** is thermodynamically analyzed in order to find a method that can reduce losses of available energy in the cryogenic system.

This system can be divided into two subsystems: a processing subsystem in which the distillation column itself is involved, and a heat exchange subsystem consisting of heat exchangers. It is assumed that the feed and products are in vapor phase and their temperatures and pressures are the same. Further assumptions are that there is neither heat loss nor friction, and that kinetic and potential energies are negligible. Since there exists neither pressure change nor chemical reaction in the system, terms related to pressure change and chemical reaction in Eq. (5) can be neglected. Equation (6) can be applied to the system by neglecting available energy change related to the second integral of Eq. (5). **Figure 3(a)** shows the heat availability lines for the heat sink and source streams in the system where no cold is recovered. Identification numbers on the diagram are those of the heat sink and source streams as shown in **Fig. 2**. The total heat of the heat sink streams is equal to that of the heat source streams. **Figure 3(b)** can be constructed by collecting stream segments with the same value of the temperature function and making up corresponding composite lines.<sup>1)</sup> The area enclosed between the composite heat source line and the dead-state line shows the increase in available energy of the heat source streams. The area enclosed between the composite heat sink line and the dead-state line shows the decrease in available energy of the heat sink streams. The latter area is larger than the former. To find the heat exchangeability of the system, the composite heat sink line is plotted directly underneath the composite heat source line as shown in **Fig. 4(a)**. This diagram shows heat availability in the cryogenic system. The heat can be transferred through a heat exchanger by matching a heat source stream with a heat sink stream, and at the same time available energy released from the heat sink stream is degraded. Heat and available energy in any cryogenic system flow in opposite directions. Consequently, the area enclosed between the composite lines corresponds to the loss of available energy due to irreversibility associated with heat transfer. In addition to the heat transfer loss, there is another loss of available energy in the processing subsystem, shown in **Fig. 4(b)**. The

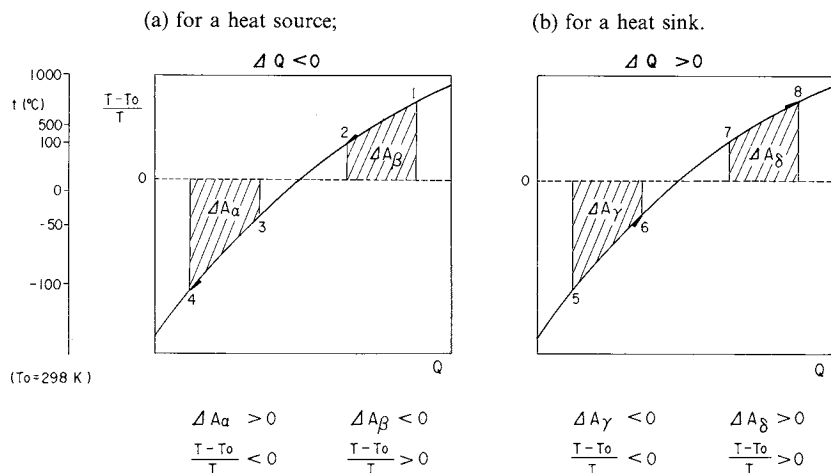


Fig. 1. Heat availability diagram.

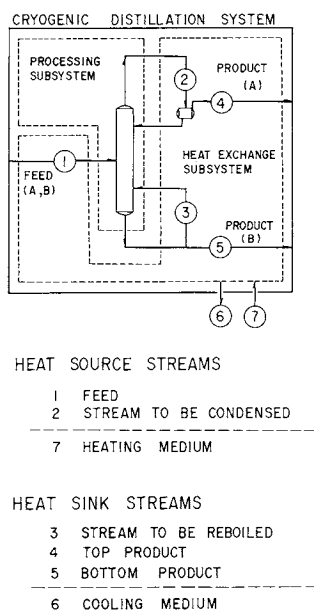


Fig. 2. A cryogenic binary distillation system.

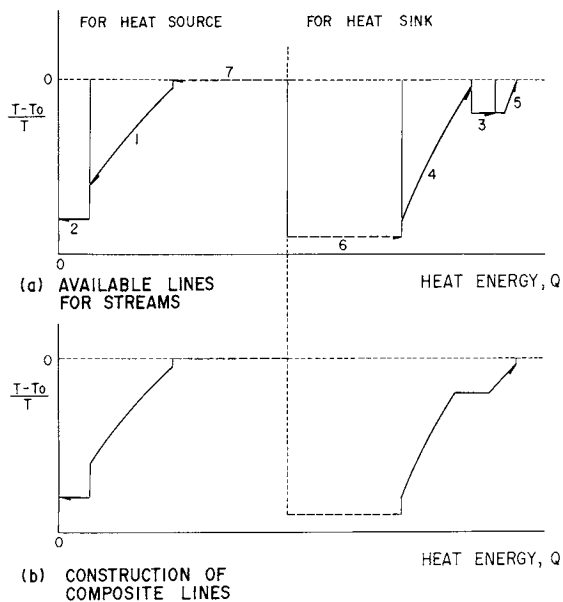


Fig. 3. Heat availability diagram.

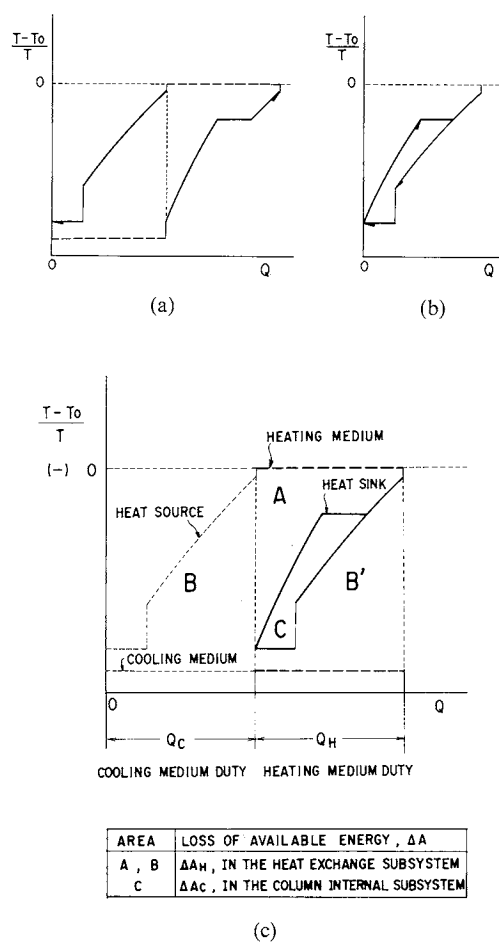


Fig. 4. Available energy loss.

(a) heat exchange subsystem; (b) processing subsystem; (c) complete system.

figure can be constructed by plotting the composite heat sink line (without the cooling medium) underneath the composite heat source line (without the heating medium). This diagram represents the available energy balance in the processing subsystem. The

area enclosed between the two composite lines shown in Fig. 4(b) expresses the sum of the loss of available energy due to irreversibility associated with distillation and the theoretical minimum work of separation  $W_m$  which corresponds to the available energy balance of the feed and products around the system at the temperature of the dead-state. Figure 4(c) represents the available energy balance in the cryogenic system. This diagram is constructed by combining the heat availability diagrams for both subsystems. The sum of  $W_m$  and the above-mentioned losses of available energy corresponds to the available energy difference between the cooling medium and the heating medium. As the result of analysis, it is stated that available energy changes including  $W_m$  in the system can be accounted for by using Eq. (6), and that a decrease in available energy loss in the cryogenic system is achieved by decreasing the area enclosed between the composite lines in the heat availability diagrams for the subsystems.

To find the effects of change in operating variables on the loss of available energy, sensitivity analysis is carried out by perturbing major operating variables of the system such as the reflux ratio,  $R$ ; the  $q$ -value of the feed at the column inlet; the operating pressure,  $P$ ; and the operating temperature,  $T$ . The results are very similar to those of the authors' earlier paper except for those of increase in operating pressure.<sup>1)</sup> The effects of increase in  $q$ -value are illustrated in Fig. 5 by shifting segments of the composite lines in the direction indicated with arrows on the heat availability diagrams. The operating variables are perturbed so as to decrease in the losses of available energy in the processing subsystem. Two types of effects appear. One is the effect of increase in loss of available energy in the heat exchange subsystem while the total loss of available energy in the system does not change. Effects of increase in  $q$ -value and local temperature change belong to this type. The total loss of available energy itself could be reduced by decreasing the loss of available energy in the heat exchange subsystem as described in the next paragraph. The other type is the effect of decrease in the loss of available energy in the system and the heat exchange subsystem. Effects of decrease in  $R$  and increase in  $P$  belong to this type. As the results of the analysis, the effects of change in the operating variables on the loss of available energy in the cryogenic binary distillation system are made clear.

### 3. Heat Integration

For a given set of information on initial structures, and design or operating conditions for a process system without heat integration, the synthesis problem is defined as the determination of heat integration schemes which minimize the loss of avail-

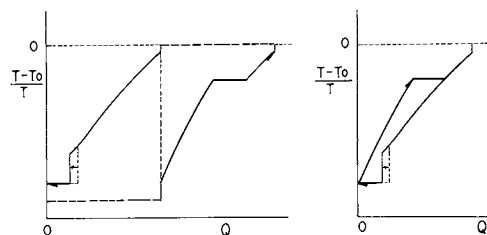


Fig. 5. Effects of increasing  $q$ -value.  
(a) heat exchange subsystem; (b) processing subsystem.

able energy in the system. To synthesize systematically the heat integration schemes, the three basic operations,  $f_P$ ,  $f_T$  and  $f_E$ , in the heat availability diagrams presented in the authors' previous paper can be effectively utilized in the same way.<sup>6,8)</sup> A pinch-point that shows the maximum rate of heat recovery can be found by using the operation  $f_E$  which shifts the composite heat sink line to the left in the heat availability diagram for the heat exchange subsystem in the system.<sup>6,8)</sup>

By repeating each set of operations ( $f_P$  and  $f_E$ ) and ( $f_T$  and  $f_E$ ) on the composite lines on their segments, a series of heat integration systems is evolved as a result of eliminating the pinch-point that occurs in each operation.<sup>6,8)</sup> The loss of available energy in the cryogenic system decreases monotonically along the repetitive operations. On the basis of the basic operations in the heat availability diagrams, a procedure for the heat integration method is presented in Fig. 6. It is a partial modification of the procedures presented in the authors' papers.<sup>6,8)</sup> From the authors' experience in designing cryogenic systems, sometimes there is no pinch-point in the heat availability diagrams for a cryogenic system. In such a case, it is necessary to change a set of design and operating conditions of the system in order to make the system approach a reversible one more nearly. Consequently, a step related to no pinch-point is added to the procedure, and an example is shown later.

The present approach can be applied in the same way to systems which have any temperature range. From a practical viewpoint, the approach can be applied to a system or its subsystems. If it is applied independently to each subsystem in a complex system, upper-level coordinations between the subsystems should be made. A complex system having unit and stream temperatures both above and below ambient temperature can be divided into two subsystems, i.e., one subsystem with temperatures higher than ambient temperature and the other subsystem with cryogenic temperatures.

### 4. Example

As a process system to be heat-integrated, the

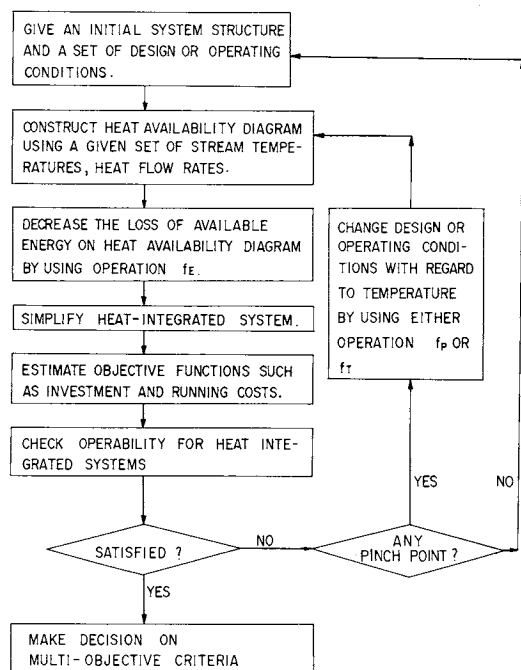


Fig. 6. Procedure of heat integration.

cryogenic demethanizer system shown in Fig. 7 is considered. The history of gas processing has been characterized by a rapid evolution over the late 60 years in order to recover ethane efficiently under minimum entropy production.<sup>4)</sup> During this period, a variety of process configurations has been tried to achieve the objective at the expense of system simplicity. It is intended in this example to show how appropriate systems can be evolved by the proposed method. The repetitive operations are shown in Fig. 8, where a set of heat availability diagrams with process flow networks is shown with the operations applied in every step. Starting from the original distillation system without heat integration shown in Fig. 8(a), three distillation systems are synthesized. One is the distillation system shown in Fig. 8(b) which requires no change in heating and cooling duties, and requires power input of 742 kW from outside the system. This system has no pinch-point, and there is a large amount of available energy losses in the heat exchange subsystem. According to the modified procedure, it is necessary to change a set of design or operating conditions to reduce further the available energy losses. In a practical sense either maximum recovery of ethane at a given power input or minimum power input at a given recovery of ethane is desired. If one wants to minimize further the loss for a given recovery rate of ethane, the design or operating conditions of the system are changed, and the other two alternative systems will be synthesized as described below. One is the distillation system shown in Fig. 8(e). Compared with that shown in Fig. 8(b), this system can reduce power input from 742 kW to

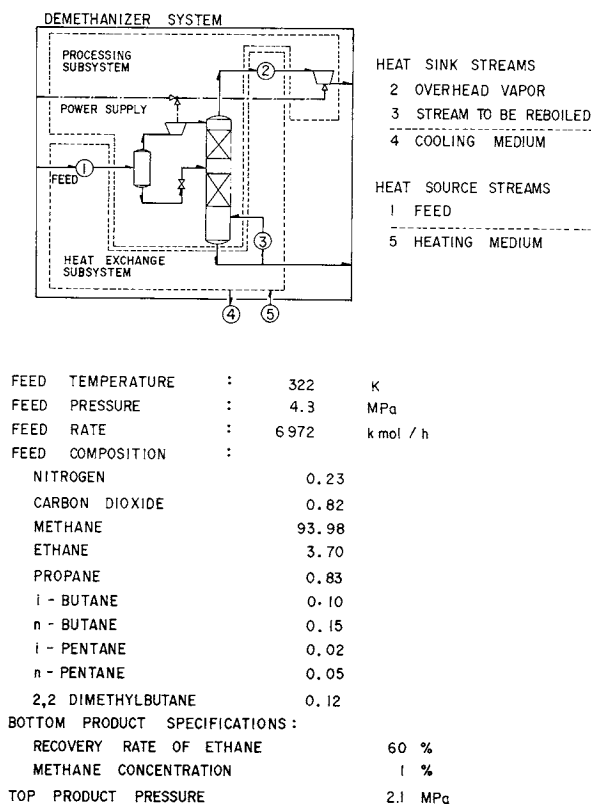


Fig. 7. Illustrative example, Demethanizer.

—1377 kW, where the heating and cooling duties are unchanged. The other is the system shown in Fig. 8(h). Compared with the system shown in Fig. 8(b), this system can reduce the amount of cooling duty from zero value to —6.93 GJ/h where no amount of power input is reduced. This reduced duty could be utilized as a refrigeration duty for other process systems. In practical application of the proposed method, the final decision on choosing the best system depends on engineering judgements considering other criteria at the same time.

## Conclusion

By using heat availability diagrams, the heat availability of process systems with unit and stream temperatures above and below ambient temperature can be analyzed. The loss of available energy and the maximum theoretical rates of heat recovery in the systems are made clear in the diagrams. Starting from an initial structure of the system without heat integration, a series of bottlenecks in heat recovery are sequentially found by a thermodynamic analysis using the diagrams and modified systems are evolved as the results of repetitive debottlenecking.

## Acknowledgment

The authors are indebted to Chiyoda Chemical Engineering and Construction Company for the support of this research work and

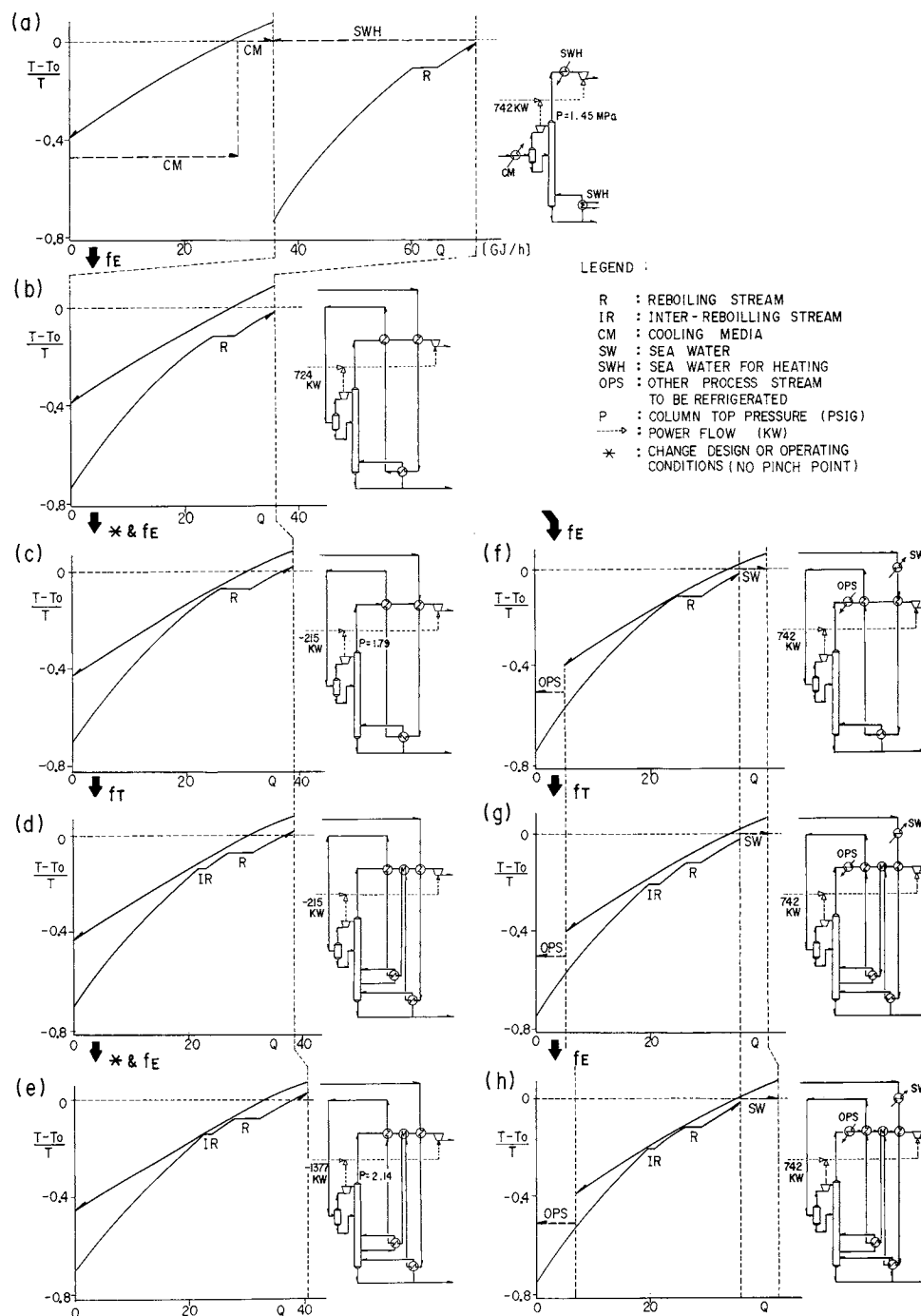


Fig. 8. Illustrative example.

for permission to publish this paper.

#### Nomenclature

$A$	= available energy	[J/h]
$H$	= enthalpy flow	[J/h]
$P$	= pressure	[Pa]
$Q$	= heat flow	[J/h]
$S$	= entropy flow	[J/Kh]
$T$	= absolute temperature	[°C]
$V$	= volume flow of a mixture	[m <sup>3</sup> /h]
$n_i$	= mole flow rate of $i$ -th component	[kmol/h]
$\mu_i$	= chemical potential of $i$ -th component	[J/mol]

#### <Subscripts>

$i$	= $i$ -th component
0	= dead state

#### Literature Cited

- 1) Itoh, T., K. Niida, K. Shiroko, T. Umeda: *Int. Chem. Eng.*, **20**, 379 (1980).
- 2) Kameyama, H., K. Yoshida: *Kagaku Kōgaku*, **43**, 390 (1970).
- 3) Keenan, J. H.: *British J. of Applied Physics*, **2**, 183 (1951).
- 4) McKee, R. L.: "Evolution in Design," Preprint of 56th Annual GPA Convention, March 21-23, 1977, Dallas, Texas.
- 5) Nishio, M., J. Itoh, K. Shiroko, T. Umeda: *Ind. Eng. Chem. Process Des. Dev.*, **19**, 306 (1980).

- 6) Shiroko, K.: Ph. D. Thesis, Tokyo Institute of Technology (1982).  
7) Umeda, T., T. Harada, K. Shiroko: *Comp. & Chem. Eng.*, **3**,

- 273 (1981).  
8) Umeda, T., K. Niida, K. Shiroko: *AIChE J.*, **25**, 423 (1979).

## SALT EFFECTS ON VAPOR-LIQUID EQUILIBRIA FOR VOLATILE STRONG ELECTROLYTE-WATER SYSTEMS

TAKESHI SAKO, TOSHIKATSU HAKUTA AND HIROSHI YOSHITOME

*National Chemical Laboratory for Industry, Yatabe, Ibaraki 305*

**Key Words:** Phase Equilibrium, Electrolyte Solution, Salt Effect, Correlation, Hydrogen Chloride, Magnesium Chloride, Calcium Chloride

Vapor-liquid equilibria for the  $\text{HCl-H}_2\text{O}$ ,  $\text{HCl-H}_2\text{O-MgCl}_2$  and  $\text{HCl-H}_2\text{O-CaCl}_2$  systems were measured under atmospheric pressure. A new method is proposed to correlate the salt effect on vapor-liquid equilibrium for the volatile strong electrolyte-water system, and a comparison between experimental and calculated results is made for the  $\text{HCl-H}_2\text{O-salt}$  and  $\text{HNO}_3\text{-H}_2\text{O-salt}$  systems. The new method is confirmed to be useful for correlating the salt effect on aqueous electrolyte solutions.

### Introduction

There is growing interest in concentration of dilute aqueous solutions of volatile strong electrolytes. Most of these solutions, such as  $\text{HCl-H}_2\text{O}$ ,  $\text{HNO}_3\text{-H}_2\text{O}$  and  $\text{HI-H}_2\text{O}$  systems, have maximum azeotropes so that it is difficult to concentrate the volatile solutes by means of a conventional distillation. When a salt is added into such systems, it may act as a separating agent in distillation. This is due to the fact that the concentration of volatile strong electrolyte in the vapor phase increases with salt content. In view of this practical importance in concentrating the volatile strong electrolyte, it is desired to obtain vapor-liquid equilibrium data and to establish an appropriate solution model which can be applied to the ternary systems composed of volatile strong electrolyte, water and salt. Vapor-liquid equilibrium data for these aqueous systems have already been reported<sup>3,6,14,17-19)</sup> and some correlations have been made<sup>2,8,9)</sup> for evaluation of the salt effect. However, the data are limited to the narrow concentration regions of volatile strong electrolyte and salt, and the correlations reported previously often give poor results for systems having a large discrepancy from ideality.

In the present study, the vapor-liquid equilibria for the  $\text{HCl-H}_2\text{O}$  and  $\text{HCl-H}_2\text{O-salt}$  systems were mea-

sured under atmospheric pressure. Furthermore, a new attempt is made to correlate the salt effect on the vapor-liquid equilibria for systems having a large discrepancy from ideality. The applicability of this method is examined for six ternary systems containing  $\text{HCl-H}_2\text{O-salt}$  and  $\text{HNO}_3\text{-H}_2\text{O-salt}$ .

### 1. Experiment

#### 1.1 Apparatus and procedure

The Othmer-type equilibrium still shown in Fig. 1 was used to obtain vapor-liquid equilibrium data. The volume of the still was about  $500\text{ cm}^3$ , of which about  $350\text{ cm}^3$  was occupied by liquid phase, and that of the vapor-phase sampling cell was about  $10\text{ cm}^3$ . The pressure was controlled at  $101.3 \pm 0.07\text{ kPa}$  through the buffer tank ( $50,000\text{ cm}^3$ ) by manual operation and was measured by a mercury manometer. The equilibrium temperature was measured within  $\pm 0.1\text{ K}$  by a thermistor thermometer calibrated by a standard thermometer. After circulation for about 4 h, the equilibrium temperature was measured and samples of the liquid and vapor phases were withdrawn from the equilibrium still and the vapor-phase sampling cell to determine the compositions of both phases.

To check the consistency of the experimental apparatus, the vapor-liquid equilibrium for the  $\text{HNO}_3\text{-H}_2\text{O}$  system was measured under atmospheric pressure and was in good agreement with the literature data.<sup>5)</sup>

Received June 15, 1983. Correspondence concerning this article should be addressed to T. Sako.