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(Vaporization Mechanism  
of Organic Contaminants)

(計 画 中)



# Studies on the Vaporization Mechanisms of Organic Pollutants in an Evaporator

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Evaporation experiments were conducted for better understanding the vaporization mechanisms of organic pollutants in brine. In this study, n-octadecane, bromoform, toluene and fuel oil A, mixed or dissolved in brine, were used as pollutants and it was examined whether the equation for steam distillation was applicable to predict the vaporization mechanisms of these substances in an experimental evaporator. As a result, we established a modified equation which could be comprehensively applied to the vaporization of not only insoluble but also soluble pollutants.

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## SYMBOLS

$W_o$  : weight of a vaporized pollutant, g

$W_w$  : weight of vaporized water, g

$M_o$  : molecular weight of a pollutant

$M_w$  : molecular weight of water

$P$  : vapor pressure, mmHg

$P_o$  : vapor pressure of a pollutant, mmHg

$P_w$  : vapor pressure of water, mmHg

$p_o$  : partial pressure of a pollutant, mmHg

$V_o$  : vaporization rate of a pollutant, g/min.

$V_w$  : vaporization rate of water, g/min.

$x$  : mole fraction

$\gamma$  : activity coefficient

$C$  : concentration of a pollutant in the brine, mol/l

$H$  : Henry's constant, mol/l, mmHg

$L$  : volume of the brine, ml

$T$  : temperature in the evaporator, °C

## INTRODUCTION

In recent years, marine pollution has been one of the major environmental concerns throughout the world. This concern is not only about an ecological problem but also about a possible crisis in the daily life of ordinary people, especially in gulf countries where greater part of the drinking water is produced by seawater desalination plants

[1,2].

In the case of MSF(multi-stage flash process) desalination plants, when operated with polluted seawater, there are mainly two concerns, i.e. (1) the pollutants may decrease the performance of the desalination process due to adhesion to the inside of the equipment, and/or (2) the pollutants may contaminate the product water and affect its quality. Since the second concern is related to the health of the people who use the water produced by the plants, the matter must be treated with greater sense of urgency and seriousness.

In this situation, a computer simulation method will be useful that can predict the quality of product water from MSF plants, when seawater feed is polluted. However, a number of technical breakthroughs are required for developing this method, such as understanding of their vaporization behaviors, estimation of adhesion effect to inner walls, and etc. Among them, development of calculation methods that describe vaporization behaviors of pollutants in brine is considered as one of the most important fundamental progresses, and in the past, only a limited number of reports have been published that is concerned about this [3, 4]. Qualitative behaviors of fuel oil A mixed with brine was studied by us using an experimental evaporator [3]. Sako et al. applied the equation for steam distillation for calculating the vaporized amount of pure insoluble chemicals in pure water [4].

This paper describes the results of a more detailed and comprehensive studies conducted on the carry over of organic pollutants in distillates from brine solutions in heterogeneous as well as homogeneous mixtures under selected flashing conditions. New mathematical formulas were suggested to help predict the evaporation mechanism of dissolved as well as insoluble complex pollutants present in brine in an evaporator.

## MATERIALS AND METHODS

### MATERIALS

n-Octane and n-octadecane were used as model insoluble pollutants. Bromoform and toluene were used as model soluble pollutants. In order to study the behavior of complex pollutants, fuel oil A was used. The artificial brine was made by adding 41g of NaCl and 30g of Instant Ocean(Aquarium Systems Inc., U.S.A.) to 1l of water. n-Hexane was used to extract bromoform from the brine in the bromoform-fuel oil A mixture evaporation experiment and carbon tetrachloride was used to extract the other organics. All the chemicals and reagents used in this study were of the reagent grades and/or chromatographic purity.

Fig. 1 shows the experimental evaporator used in this study. This was composed of a rotary evaporator including a condenser, a water bath, an impinger, a vacuum pump, a manometer, a controlled water circulator and tubings(Shibata Scientific Instruments, Japan).

For the quantitation of pollutants, gas chromatograph(GC ; Model 5880A, Hewlett Packard, U.S.A.) was used, which was connected to a purge trap(PT) autoinjector(Model LSC-2, Tekmar, U.S.A.) and an ECD detector. For the resolution of fuel oil A constituents, mass spectrometry detector(MSD ; Model 5970A, Hewlett Packard, U.S.A.) was used.

### METHODS

The evaporation conditions applied in this study were as follows. The pre-heating time to raise the temperature of the brine, was 10 minutes. The evaporation conditions were 90°C and 420mmHg in most cases and the flask was rotated at 50rpm. The evaporation times were from 0 to 60 min.

Procedures of the experiment were described below. First, 500ml of the brine was put into the flask and then the pollutant(s) was added in it. The flask was placed in the waterbath and incubated for pre-heating. After that, the vacuum was started and the pressure in the evaporator was maintained at 420mmHg for the desired period. The flask was removed after elapsing the time and was cooled in water.

The initial amounts of pollutants were determined by weighing, in the cases of n-octadecane and fuel oil A and by using the GC, in the cases of bromoform and toluene. The initial weight of n-octadecane in fuel oil A was calculated by using the percentage of n-octadecane in fuel oil A, i.e. 1.6%.

In the material balance experiment, the pollutants transferred into the condenser and the impinger were extracted either with n-hexane or carbon tetrachloride and quantitated with the GC. In the experiments done to obtain the vaporization rates of the pollutants, only the remaining material in the brine were quantitated. The amounts of vaporized pollutants were calculated by subtracting the weight of the remaining from the weight of the initial. The amount of vaporized water was obtained by subtracting the weight of the flask after evaporation from the initial weight of the flask.

The quantitation with GC-MSD and purge and trap/GC were conducted by following EPA's standard methods of monitoring organics in water[7,8], with minor modifications. The bromoform solutions were diluted to appropriate concentrations with HPLC water, before injection into the purge-trap injector. In the bromoform-fuel oil A mixture evaporation experiment, bromoform was extracted with n-hexane and injected into the GC directly. The concentration of toluene in the brine was determined with the GC-MSD after extraction with n-hexane.

## RESULTS

## MATERIAL BALANCE EXPERIMENT

In order to evaluate any possible experimental errors in the evaporation procedures, material balance experiment was first carried out. After conducting an evaporation experiment as described above, the amounts of pollutants which transferred to the impinger, to the condenser, which remained in the brine were quantitated by the methods described above and the total amount was compared with the initial amount.

Table 1 shows the results of these experiments. In these experiments, total recoveries were between 90 to 112% of the initial, and, therefore, it was ascertained that there were no considerable amounts of evaporation losses of the organics during the evaporation process. Consequently, it was considered that the amount of vaporized pollutants could be obtained by measuring the remaining amount in the brine and subtracting it from the initial amount.

## VAPORIZATION OF SINGLE n-OCTADECANE

n-Octadecane is one of the major components in fuel oil A. The solubility of n-octadecane in water is below 10ppb[6,7], and in our experimental conditions (Table 2), almost all n-octadecane was thought to be insoluble and stand independently of the brine(i.e. heterogeneous system).

In the case where n-octadecane-contaminated brine was evaporated, the equation for steam distillation which is described below was considered to be most suitable for calculating the amount of vaporized n-octadecane :

$$\frac{W_o}{W_w} = \frac{M_o \cdot P_o}{M_w \cdot P_w}$$

This equation was previously applied to the vaporization of volatile hydrocarbons at high



concentration, by Sako et.al.[4]. In that paper, the proportional relationships between  $W_w$  and  $W_o$  were obtained and the proportionality constants ( $W_o/W_w$ ) obtained from the experiment agreed well with the calculated ratios of  $M_o \cdot P_o / M_w \cdot P_w$ .

Here, we conducted vaporization experiments with n-octadecane-contaminated brine and  $W_w$  and  $W_o$  were measured under different conditions (Table 2). In this case, a proportional relationship between them was also obtained (Fig. 2). From this data,  $R(W_o/W_w)$  and the vapor pressure of n-octadecane were obtained as  $1.1 \times 10^{-3}$  and  $4.2 \times 10^{-2}$  (mmHg), respectively. It is also shown in the table that the amounts of vaporized n-octadecane ( $W_o$ ) do not change significantly when its initial amounts in the brine are varied, keeping other evaporational conditions constant.

Furthermore, the ratio 'R' were compared under different total pressures. As shown in Table 2, the evaporation experiments at pressure of 500 mmHg were carried out where other conditions were the same. As a result, R was obtained as  $1.3 \times 10^{-3}$  at the above pressure, that was similar with the value at 420 mmHg.

#### VAPORIZATION OF BROMOFORM

In order to apply the equation for steam distillation to dissolved pollutants (homogeneous system), we developed a modified equation as described below. When the vaporization rates of a dissolved pollutant and water are represented as  $V_o$  and  $V_w$ , respectively, the equation for steam distillation can be revised as below :

$$\frac{M_o \cdot P_o}{M_w \cdot P_w} = \frac{W_o}{W_w} = \frac{V_o \cdot t}{V_w \cdot t} = \frac{V_o}{V_w} = R \quad \text{----- (1)}$$

In this equation,  $M_o$ ,  $M_w$ ,  $P_w$  are the constants and from the previous experiment  $V_w$  is

also considered as a constant. R is the proportional constant. However,  $P_o$  for dissolved materials is known to be ruled by Henry's law (equation(2)) :

$$C_o = H_o \cdot P_o \text{ ----- (2)}$$

Therefore, when  $C_o$  changes by time,  $P_o$  becomes a function against time and equation(1) is revised as below ;

$$V_o(t) = \frac{V_w \cdot M_o}{M_w \cdot P_w} P_o(t) = \frac{V_w \cdot M_o}{M_w \cdot P_w} \cdot 1/H \cdot C_o(t) = R' \cdot C_o(t) \text{ ----- (3)}$$

$$R' = \frac{V_w \cdot M_o}{M_w \cdot P_w \cdot H} \text{ ----- (4)}$$

Therefore, in the case of a batch evaporator, the concentration of the dissolved pollutant at time 'x' can be described as follows:

$$\begin{aligned} C_o(x) &= C_o(0) - \int_0^x V_o(t) dt \\ &= C_o(0) - \int_0^x R' \cdot C_o(t) dt \text{ ----- (5)} \end{aligned}$$

From this differential equation, we obtain equation(5) and (5'):

$$C_o(t) = C_o(0) \cdot e^{-R' t} \text{ ----- (6)}$$

$$\ln C_o(t) = \ln C_o(0) - R' t \text{ ----- (6')}$$

By applying this equation to equation(1) and (2),  $W_o(t)$  is obtained as follows :

$$W_o(t) = L \cdot C_o(0) \cdot (1 - e^{-R' t}) \text{ ----- (7)}$$

Here, evaporation experiments were carried out with the batch evaporator to examine whether the above equations could be applied to dissolved pollutants. Bromoform is a kind of trihalomethane and is known to be often detected in seawater and especially in chlorinated seawater of desalination plants at high concentrations. This is a highly

soluble organic compound. Its solubility in pure water is quite considerable(800ppm) and in our observation the solubility in the brine was approximately 300ppm. Therefore, in this study, bromoform was used as one of the typical dissolved pollutants, in order to check the validity of applying the above equations for the evaporation of soluble organics in brine (i.e. homogeneous system).

The evaporation experiments using the bromoform contaminated brine at the concentration of about 0.4ppm were carried out by varying the vacuum time. In this experiment, the concentration of bromoform remaining in the brine after evaporation was measured by PT-GC-ECD technique and corrected by calculating the initial concentration as 0.4ppm, following equation(5). The result obtained is shown in Fig.3 and Fig.4. From these results, it is obvious that equation(5) and equation(6) are applicable to this case. Therefore, equation(1) is considered as an alternative to the equation for steam distillation in the cases of dissolved pollutants.

$R'$  in equation(3) is obtained as 0.11(1/min.) from the slope of the graph in Fig.3-B which represents the relationship between the time and  $\ln C_0$ .  $V_w$  is obtained as 0.15(mol./l,min.) in this experiment(data not shown). By applying these values to equation (4), Henry's constant for bromoform at 90°C is calculated as  $3.7 \times 10^{-2}$ (mol./l,mmHg).

#### VAPORIZATION OF TOLUENE

Toluene is contained in crude oil as a major component and is soluble in water at a concentration of less than 500ppm. Therefore, in the case of oil spillage, it dissolves in seawater and may be sucked in by intakes of desalination plants.

In our experiments, toluene concentration in the brine was approximately 2ppm where

toluene was completely dissolved in the brine. The resulted data were analyzed by the same method as that applied in the case of bromoform and the calculated values of  $\ln C_0$  vs time is shown in Fig.5. This result demonstrates that the equation described above is also applicable to the vaporization of dissolved toluene.

$R'$  for toluene is obtained as 0.62. Thus, by the same method, Henry's constant for toluene is calculated as  $2.1 \times 10^{-3}$  (mol./l, mmHg), that is a value 15 times lower than that of bromoform. These figures rightly show that toluene is more volatile than bromoform.

#### VAPORIZATION OF n-OCTADECANE IN FUEL OIL A

The experiments described above are concerned with various single pollutants. However, in considering an actual oil spillage, we recognize that the vaporization mechanism of a complex pollutant must be understood. In such a case, it is natural to conclude that some modifications are necessary in order to apply the rule established in the previous sections to the vaporization of a complex pollutant. Additional experiments were conducted using fuel oil A to evaluate the behaviour of a single component in the presence of a complex mixture.

The evaporation experiment of fuel oil A was carried out in the same manner as that of pure n-octadecane, to measure the vaporized n-octadecane, which is one of the major components of fuel oil A. The resulted chromatograms of residual components in the brine at different evaporation times are presented in Fig.6, where all the major peaks are due to normal paraffins and the retention time of n-octadecane is 22.8 minutes. It can be observed in this figure that light components disappeared immediately and heavy components remained for longer periods.

Fig.7 shows the relationship between the weight of vaporized water and that of n-

octadecane in fuel oil A. In this figure, almost all n-octadecane present in the added fuel oil A was vaporized by 25min. and the proportional relationship between them was observed by about 20 min., after the vacuum was started. By using the data up to this period, the proportionality constant in the equation for steam distillation,  $R (W_o/W_w)$ , for n-octadecane as a component of fuel oil A, can be obtained as  $2.7 \times 10^{-5}$ . The partial pressure of n-octadecane in this system was also calculated and obtained as  $1.0 \times 10^{-3}$ .

## DISCUSSION

In this study, we carried out the evaporation experiments with the experimental batch evaporator using brine in which some organics had been mixed as the pollutants. As a result, it was shown that the vaporization of the insoluble pollutant, i.e. n-octadecane followed the equation for steam distillation. By using this equation, the amount of the vaporized pollutant can be obtained if the temperature and the amount of vaporized water is known. The temperature in the evaporator must be known in order to obtain the vapor pressures of water and pollutants.

In general, the vapor pressure is calculated by using Antoine's equation [5]. However, the constants in this equation can usually be applied only to a certain range of temperature where the experiments for obtaining the constants were conducted, for example the range of the temperature for the vapor pressure of n-octadecane is from  $173^{\circ}\text{C}$  to  $316^{\circ}\text{C}$ . This time, in order to calculate the vapor pressure of n-paraffins, we applied the data obtained from Antoine's equation to Clapeyron-Clausius's equation, and the calculated result is presented in Fig.8. Clapeyron-Clausius's equation is described below ;

$$\ln P = -\frac{\Delta H}{RT} + \text{const.} \quad (\text{Clapeyron-Clausius's equation})$$

where R is the gas constant and  $\Delta H$  is the Enthalpy. In this equation, there is the linear relationship between  $\ln P$  and  $1/T$ .

By this method, the vapor pressure of n-octadecane at 90°C was calculated as  $6 \times 10^{-2}$  (mmHg). On the other hand, the vapor pressure obtained from the experiment is  $4.2 \times 10^{-2}$  (mmHg) which almost coincides with the above value.

Following the equation for steam distillation, two important rules must be recognized. The first is that the ratio 'R' ( $W_o/W_w$ ) is not influenced by the total pressure of the vapor phase. This was demonstrated by the experiments with n-octadecane that were carried out at two pressures and comparisons were made of the 'R'.

The second is that the vaporization rates of insoluble pollutants are constant and independent of the amount in the brine. This is also shown in the data in Table 2, and therefore, it is considered that insoluble pollutants vaporize at constant rates till all of them disappear. In this case, the amount of the vaporized pollutant ( $W_o$ ) is in proportion to time in the same way with the amount of vaporized water ( $W_w$ ).

However, dissolved pollutants vaporized in a different manner. As shown in Fig. 3 - 5, it was demonstrated that the vaporization of dissolved pollutants in the batch evaporator followed the exponential function as represented by equation (6) or equation (7). It was shown in this study that the amount of a vaporized dissolved pollutant in an evaporator can be calculated by using these equations. As a result, in the cases of soluble pollutants, the equation for steam distillation can be modified by applying Henry's law and equation (1), as presented below :

$$\frac{V_o}{V_w} = \frac{M_o \cdot C_o / H_o}{M_w \cdot P_w}$$

However, Henry's constants for many organics have not been known, especially for trihalomethanes, which have been detected in feed seawater of MSF plants in many cases [2]. Therefore, it is necessary to measure Henry's constants for some trihalomethanes.

The vaporization of a complex pollutant was also studied in order to compare the vaporization rate of a component of a complex pollutant and the rate where the component existed singly. When n-octadecane existed as the single contaminant in the brine, the vapor pressure was obtained as  $4.2 \times 10^{-2}$ , whereas in the case where n-octadecane was one component of fuel oil A, the partial pressure was obtained as  $1.0 \times 10^{-3}$ . In this case, it is considered that n-octadecane is one dissolved component of a complex mixture, i.e. fuel oil A. Therefore, modified Raoult's law, described below, which is modified so as to be applied to practical solutions, is used to obtain the partial pressure of the component :

$$p_i = x_i \cdot P_{oi} \cdot \gamma_i$$

From this equation and the modified equation for steam distillation, the following equation is obtained that describes the vaporization of a complex pollutant in an evaporator.

$$\frac{V_{oi}}{V_w} = \frac{M_{oi} \cdot P_{oi} \cdot x_i \cdot \gamma_i}{M_w \cdot P_w}$$

The mole fraction of n-octadecane is calculated as approximately 0.02 from the data of gas chromatography. Therefore, when the activity coefficient is considered to be 1, R ( $V_{oi}$

$\gamma/V_w$ ) for n-octadecane in fuel oil A is calculated as  $2.1 \times 10^{-5}$ . This coincides well with the value obtained from the experiment that is  $2.7 \times 10^{-5}$ . Furthermore, if we take a more accurate value of the activity coefficient into consideration, the agreement will be better.

As described above, we carried out the evaporation experiments on the brine containing the organic pollutants and developed the fundamental equations for describing the vaporization mechanisms of pollutants in the evaporator. By using the equations, if the physical conditions, i.e. the temperature or the pressure, in an evaporator and water vaporization rate are defined, we can easily calculate the vaporization rates of pollutants in brine, in any conditions like the high temperature stages of MSF plants and the low temperature stages, and even in deaerator.

Our final goal is to develop a computer simulation program for predicting the quality of product water of MSF plants, when feed seawater is polluted. We expect that the equations developed in this study can be applied to fundamental parts of the program. However, taking the actual MSF plants into consideration, we realize the necessity of further studies on the condensation mechanism of vaporized materials. Besides, some studies may also be required to estimate effects of adhesion of pollutants to inner walls of the facilities such as heat transfer tubes. The program will be accomplished by gathering these results together and involving them in a MSF process modeling program.

## CONCLUSION

In order to develop calculation methods for estimating the vaporized amount of organic pollutants in brine in an evaporator, evaporation experiments were conducted by using



an experimental batch evaporator and artificial brine mixed with some organics or fuel oil

A. As a result, it was manifested that the equation for steam distillation was applicable for the purpose with some modifications. For describing the vaporization of soluble pollutants, the following equation was proposed.

$$\frac{V_o}{V_w} = \frac{M_o \cdot C_o / H_o}{M_w \cdot P_w}$$

In addition, it was found that the vaporization of insoluble pollutants composed of mixed components followed the equation presented below.

$$\frac{V_{oi}}{V_w} = \frac{M_{oi} \cdot P_{oi} \cdot x_i \cdot \gamma_i}{M_w \cdot P_w}$$

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Table 1 Material Balance of Pollutants after Evaporation

Pollutants	Conditions <sup>(1)</sup>	Recovery(%) <sup>(2)</sup>			
		Brine	Condenser	Impinger	Total
n-Octadecane	10ppm, 90° C	30	60	-	90
	50ppm, 90° C	84	18	1	103
	50ppm, 40° C	112	-	-	112
n-Octane	10ppm, 90° C	-	2	92	94
	50ppm, 90° C	1	1	95	97
	50ppm, 40° C	19	1	83	103
Bromoform	10ppm, 90° C	48	2	40	90
	10ppm, 40° C	85	1	12	98

(1) The evaporation was conducted for 5 minutes. The other experimental conditions that are not shown in this table are described in 'Materials and Methods'.

(2) Recovery(%) = The weight of pollutants after evaporation / The initial weight

X 100

Table 2. The Vaporization of n-Octadecane contaminated in the Brine

Evaporation period(min)	Vaporized Water(g) (Ww)	n-Octadecane(mg)		
		Initial	Remaining	Vaporized(Wo)
0	1	9	10	-
10	14	33	16	17
20	21	30	7	23
5	6	33	25	8
5	7	30	24	6
10	10	19	7	12
10	11	47	34	13
10	8	20	11	9
10	9	12	4	8
30	32	42	10	32
10 <sup>(1)</sup>	1.4	21	19	2
20 <sup>(1)</sup>	3.3	19	15	4

The experimental conditions were described in Materials and Methods.

(1) In these two experiments, the pressure in the evaporator was 500 mmHg where other conditions were same with the other experiments in this table.

## LEGENDS FOR FIGURES

Fig.1 Systematic Diagram of the Evaporator Used in This Study.

Fig.2 Single n-Octadecane Vaporization Experiment. The conditions of the experiment were described in Table 2. The evaporation period was varied in every experiment, and the amount of vaporized water and that of vaporized n-octadecane were quantitated as described in 'Materials and Methods'.

Fig.3 Time Course of Bromoform Concentration( $C_0$  : A) and  $\ln C_0$ (B) in Bromoform Vaporization Experiment. The bromoform concentration in the brine after each evaporation experiment was quantitated as described in 'Materials and Methods'.

Fig.4 Time Course of the Amount of Vaporized Bromoform in Bromoform Vaporization Experiment. The amount of vaporized bromoform was obtained by subtracting the amount of bromoform remained in the brine from the initial amount.

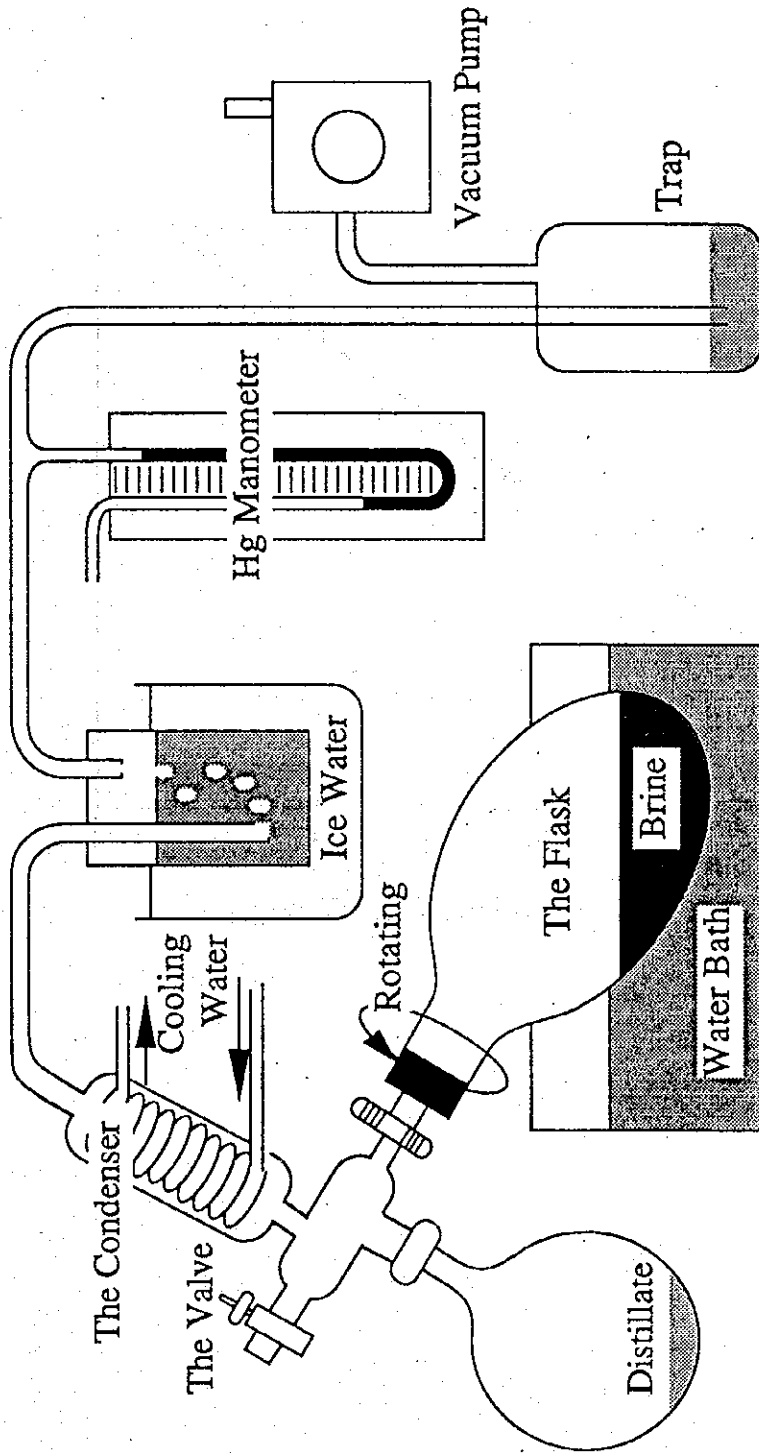
Fig.5 Time Course of  $\ln C_0$  in Toluene Vaporization Experiment. The toluene concentration in the brine after each evaporation experiment was quantitated as described in 'Materials and Methods'.

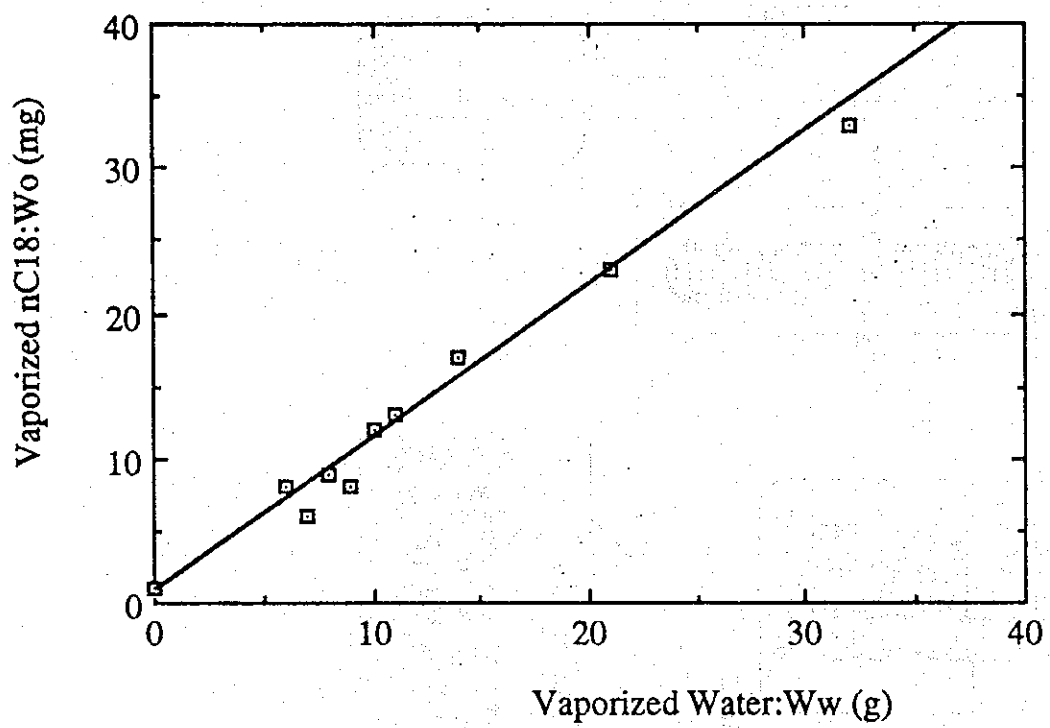
Fig.6 Chromatograms of the Residual Components in the Brine after Evaporation in Fuel Oil A Vaporization Experiment. The evaporation periods are described in the figure. The two peaks appeared at 7.5min. and 12.5min. are due to the impurities in the extraction solvent. The peak of n-octadecane is indicated with the arrow.

**Fig.7 Vaporization Experiment of n-Octadecane in Fuel Oil A.** The experiment was carried out in the same manner with the single n-octadecane vaporization experiment which is presented in Fig.2.

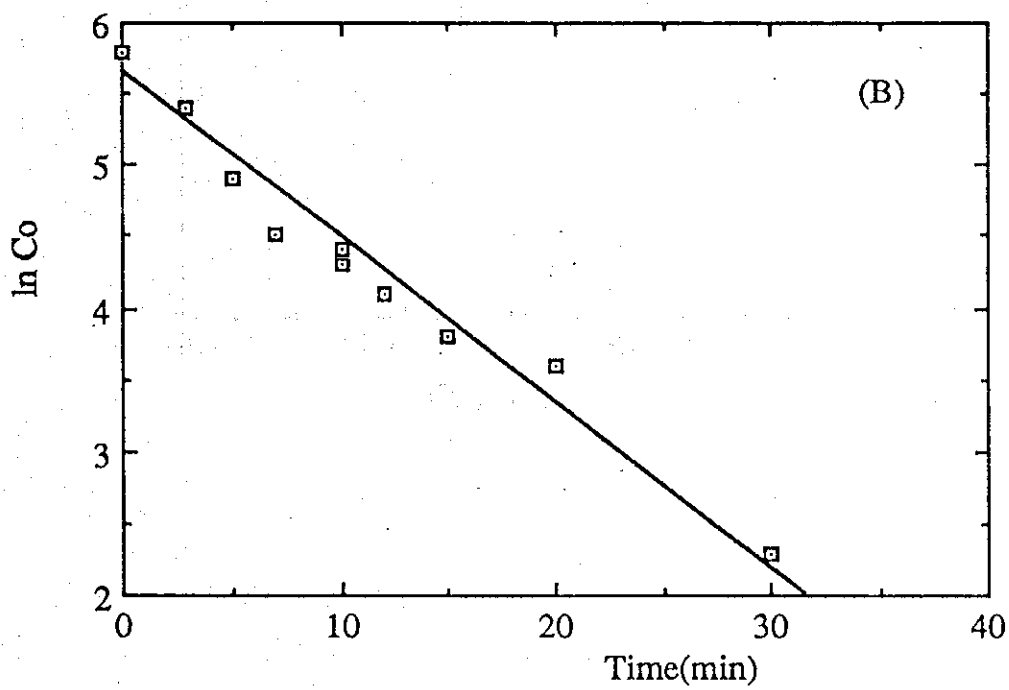
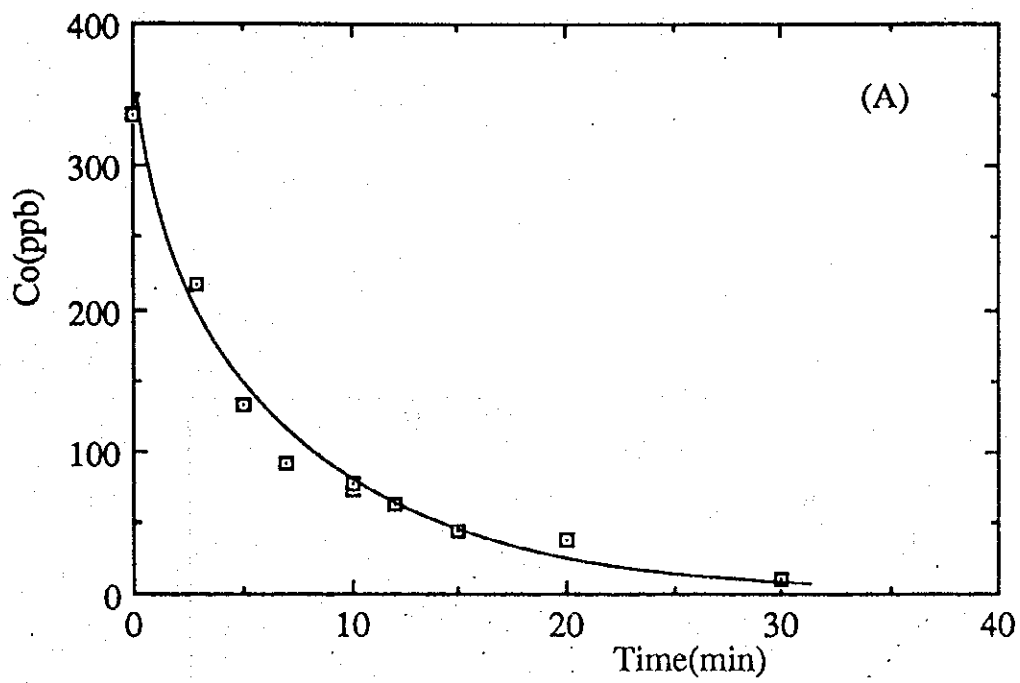
**Fig.8 Vapor Pressure of Normal Paraffins.** These were calculated as described in 'Discussion'.

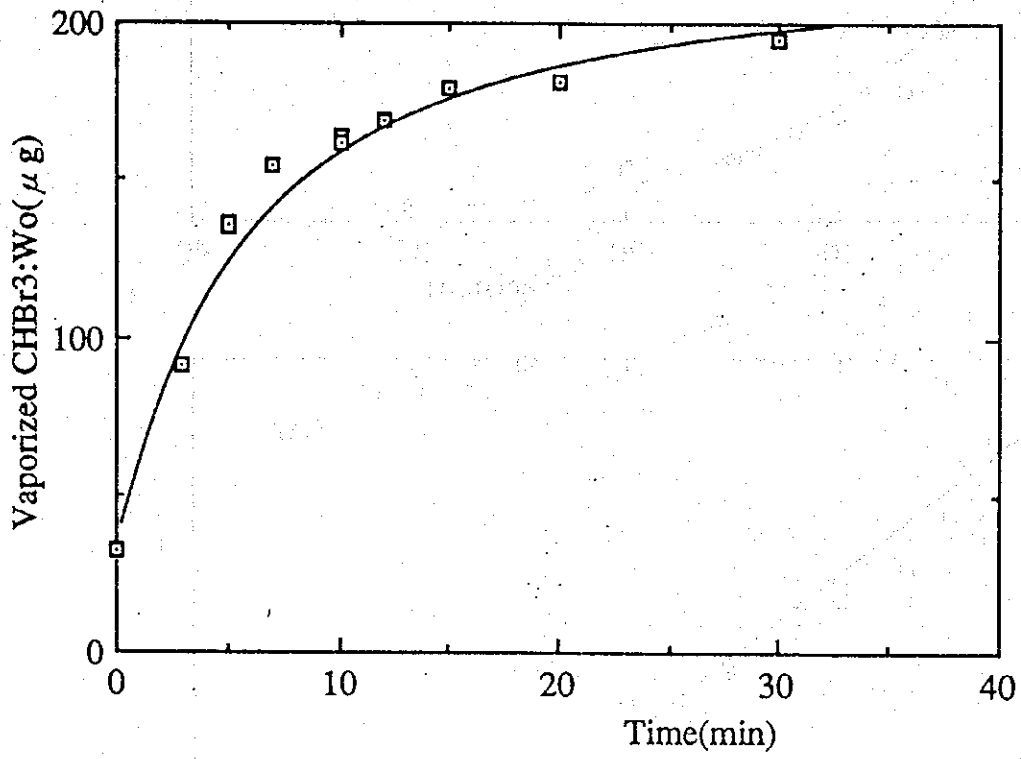
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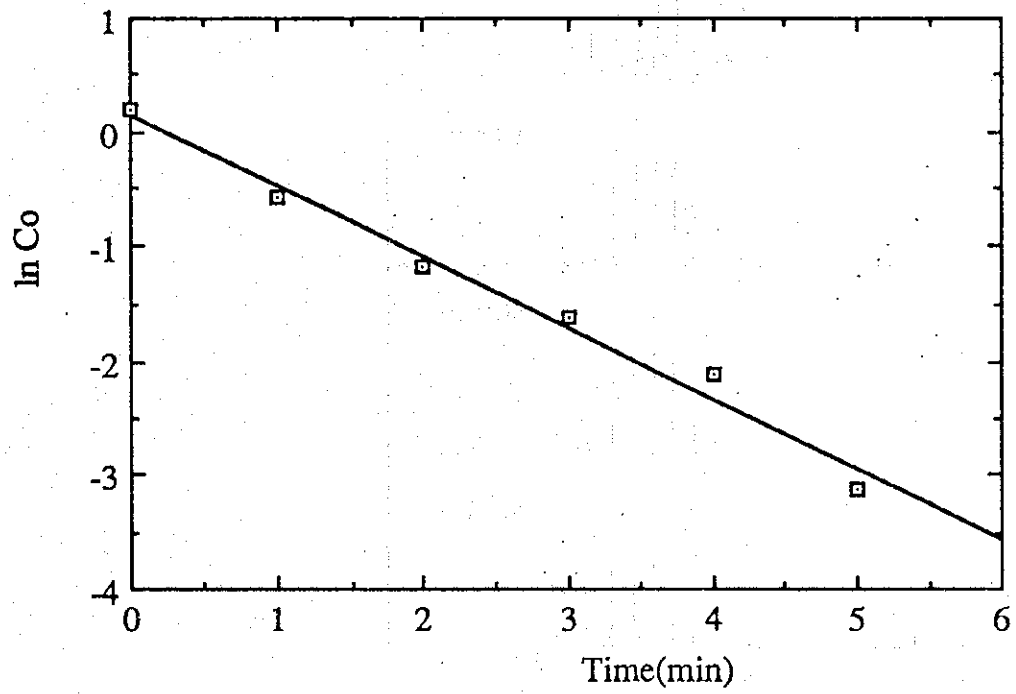


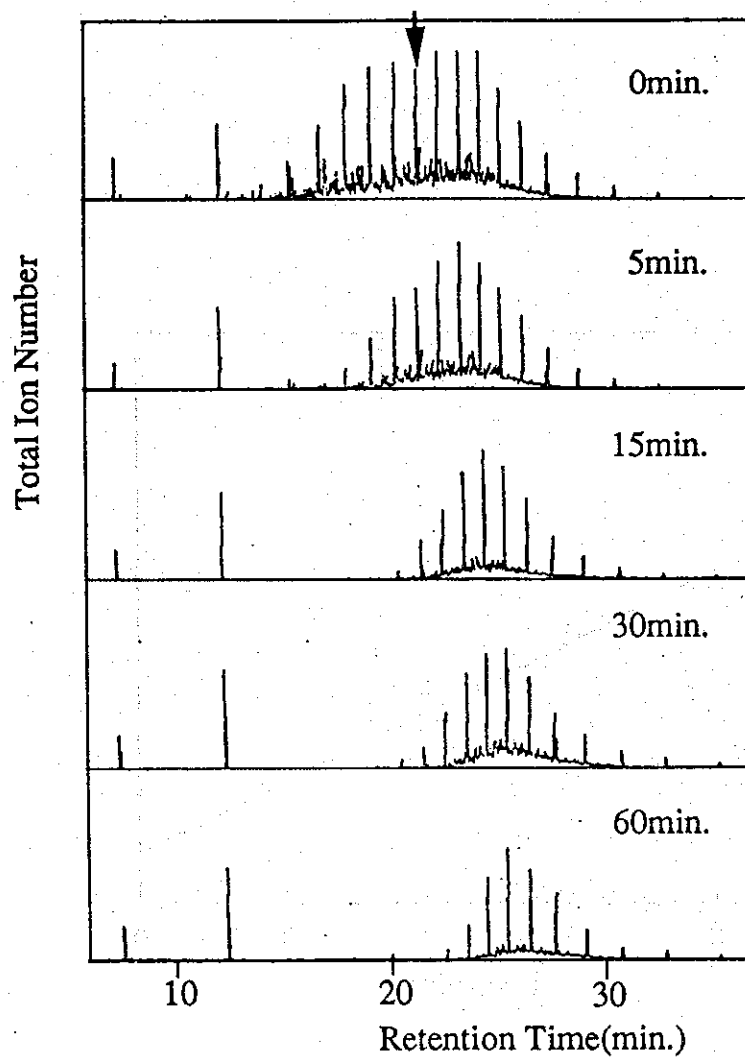


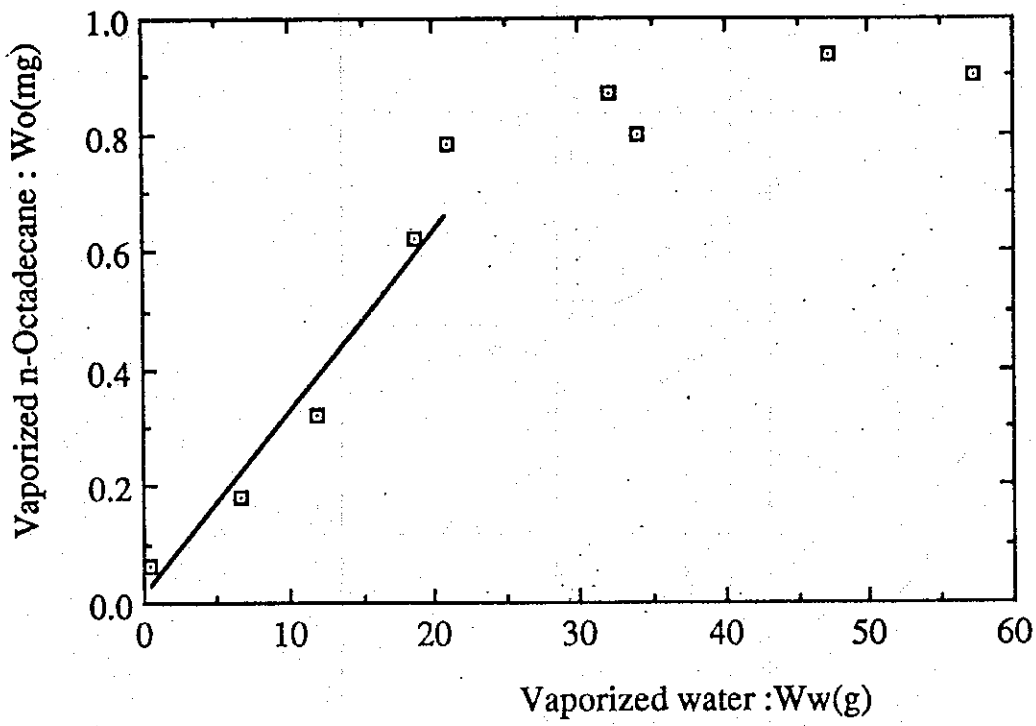


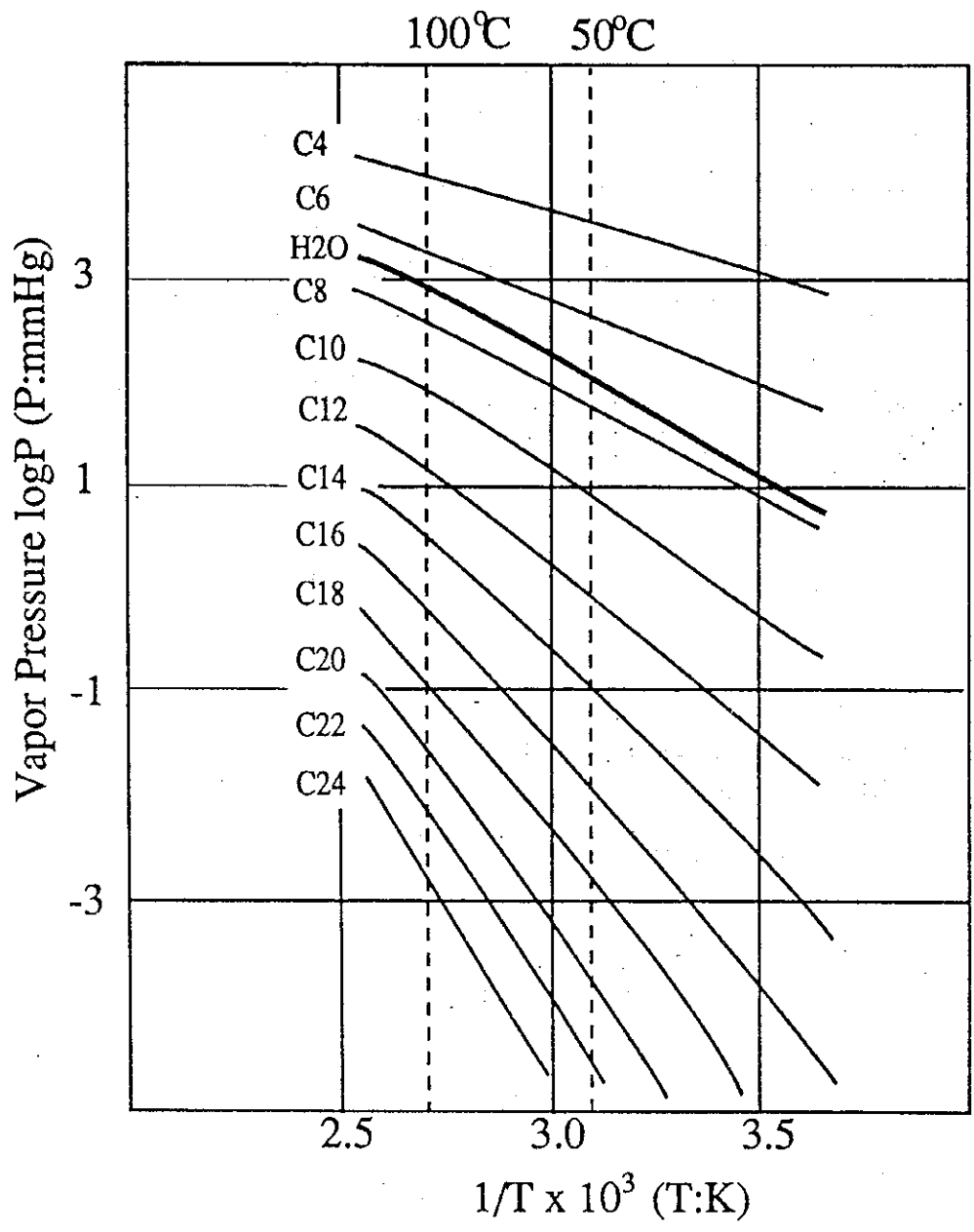












付屬資料 6.2

氣液平衡裝置運轉說明書





(Appendix 6.2)

OPERATION MANUAL OF VAPOR/LIQUID EQUILIBRIUM EXPERIMENTAL APPARATUS

Model No. R.W (Improved type)

The main components of the Vapor/Liquid Equilibrium Experimental Apparatus can be grouped into three configurations on the whole as listed below.

- (1) Equilibrium Main Equipment of the Experimental Apparatus
- (2) Measurement Operation and Control Panel
- (3) Vacuum/Pressure Reducing Exhaust System

Refer to the drawing No.1.

1.0 How to Assemble the Main Equipment of the Experimental Apparatus

listed above as item (1)

Careful attention should be given to the way of handling the glass commodity. Please see the drawing No.3 Assembly Drawing of Main Equipment.

1. Fixing fittings are provided on the panel.
2. Remove the cap screws of this fixing fittings and remove the stoppers (a), (c), (d) and (e).
3. Place the fixing fitting in-between of two access holes located on the upper section of (1) of the main equipment (on which the mantle heater is put). The section (2) and (4) are also placed on the fixing fitting.
4. Put the stopper for each of them respectively and fix the screw in the way not too strong. The step listed above will complete the fixing of the main equipment.
5. Put together the ball joint of the vapor condensing column and the joint of the equipment (4). Then, attach the fixing fitting (d) and drive the screw.
6. Put together the ball joint of the sample charging column (5) and the joint of the condensing column. And then, attach the fixing fitting (e) and drive the screw. Finally, fix the each joint nipper onto the f-1 and f-2.
7. How to attach the Vapor/atmospheric changeover cocks, (8), (9), (10), and

(Appendix 6.2)

⑪. Put these cocks on the fixing fitting (g), (h), (i) and (j) for each of them respectively, and then put them together to the joints of the main equipment by using up/down screws. After that, drive the screw to fix. Next, set and fix the sample collecting column (8'), (9'), (10') and (11') to the bottom of each of them. (Four places) This will complete fixing and assembly of articles made of glass.

CAUTION: When you assemble the ball joint and taper joint made of glass, never forget to practice to handle their inserting sections after wiping the dirt on them using alcohol and after applying a small amount of grease on the convex portion. Too much application of grease will cause an effect of measurement, so care should be taken.

8. Connect the vacuum suction connection with each of the suction port and also connect the water IN/OUT with the condensing column.

This step will complete the assembly step of the main equipment.

Connection Between Measurement Operation and Control Panel and The Main Equipment

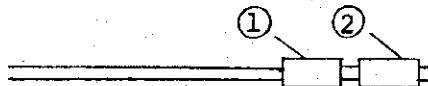
9. Electrical power supply connecting

There are two transformers attached (as listed below)

220V --- AC 100V

110V --- AC 100V

The power supply cord is as shown in the sketch below.



Section 1 and 2 can be pulled out separately.

In case of using the 110V transformer, use only the section 1.

In case of using the 220V transformer, a combinations of ① and ② are to be used.

10. See the drawing No.1 for connecting with the main equipment.

(Appendix 6.2)

Insert the heater sensor (21) into the mantle heater section (4) of the main equipment.

Insert the heater cord (22) into the mantle heater outlet (4) of the main equipment.

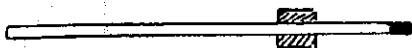
Insert the heater sensor (23) into the mantle heater section (5) of the main equipment.

Insert the heater cord (24) into the mantle heater outlet (5) of the main equipment.

Insert the still heater sensor (25) into the glass section hole (18) of the main equipment.

Insert the still heater cord (26) into the still heater (cartridge type) outlet (15) of the main equipment.

11. Insert the thermometer (1) into the upper section glass hole (4). A sili cone plug should be inserted when using this thermometer in such a manner that its end will not touch the bottom of the glass hole.



These steps will complete the connection work with the main equipment.

Vacuum/Pressure Reducing Exhaust System

12. Loosen the screws of the fixing fittings at seven places where glass parts and Dewar flask are placed, and remove the stopper (of Dewar flask only). Other sections are to be opened.

Attach the air cleaning column (9), air drying column (10) and Dewar flask (13) and drive each screw.

Insert the gas collecting column (12) into the position of fixing fitting through a hole of cork plug in the upper section of the Dewar flask and press it gently. Then, hold the fitting stopper on it and drive the screw.

13. Each section is connected using a vacuum rubber tube as shown in the drawing No.2.

Connect the vacuum suction connection (1) with the vacuum pump connection (25) using a vacuum rubber tube.

14. With the back side access door opened, put the surge tank into the inside

(Appendix 6.2)

of housing and connect the suction connection.

15. The power supply cord is to be inserted into the spare outlet (20) of the Measurement Operation/Control Panel.

All the steps listed above will complete the assembly work of all three main components.

**2.0 Preparation for the Experiment**

(See the drawing No.3)

**1. Mixing of sample**

It is important to mix the sample liquid completely. In case there exist a bubble, it is required to use it after breaking the bubble.

**2. Operation under atmospheric condition**

Set the cock (A) of (7) to the atmospheric side.

See the sketch on the right.

Close the cock (B) and open the (B').

Close the cock (C) and open the (C').

Close the cock (D) and open the (D').

Close the cock (E) and open the (E').

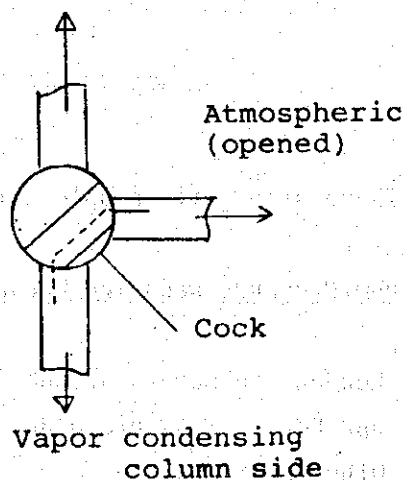
Put the sample collecting column for atmospheric condition to each of the sample collecting column (8'), (9'), (10') and (11').

Close the cock (F) to charge the sample to the sample charging column (one liter capacity).

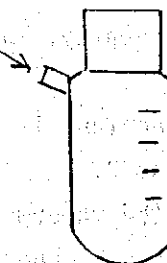
See the sketch on the right for the characteristics.

3. Open the cock (F), and the sample liquid will be fed to the inside of the Still (2). Fill the sample liquid up to the level equal to the Cottrell pump section bottom, the same level as a narrow section between the equipment

Vacuum Suction side



An air vent is provided.



(Appendix 6.2)

upper section ① and Still ②.

These steps will complete the preparation work.

### 3.0 Experiment

(See the drawing No.1 Measurement Operation/Control Panel)

1. Turn ON the main Power supply 1- ⑦ on the control panel.  
The lamp 1- ② will light.

2. Set the temperature of the temp. indicating controller 1- ⑥ and 1- ⑨ to a point a little higher than the ambient temperature. The voltage regulator 1- ⑤ and 1- ⑧ is to be turned a little bit.

Note: This can be used depending on the condition of ambient temperature at a test time and therefore, it may not be used as the case may be. This is needed especially in a cold district.

3. The temperature of the Still heater temp. indicating controller 1- ⑫ is to be set beforehand to a boiling point of sample.

4. Set the timer 1- ⑭ in such manner that the buzzer may sound at every five minutes. A sounding time of two seconds is preferable. The purpose of this buzzer is for making aware of the time coming to read the thermometer on the top of the equipment.

5. Turn ON the heater operation switch of 1- ⑦, 1- ⑩ and 1- ⑬ and also turn ON the buzzer operation switch 1- ⑮.  
Turn the knob of the voltage regulator 1- ⑪ to heat up the Still heater temperature.

Note: One of the most important things at this operation is that a sudden temperature rise is not desired and however a too slow rise is not good enough.

6. Mixed sample liquid is heated and vapor and mixed liquid are made to jet by using Cottrell pump.

7. Read and record the temperature by means of the thermometer on the top

(Appendix 6.2)

section every time the buzzer will sound. A division of this thermometer is  $0.2^{\circ}\text{C}$  and by using the magnification lens, a temperature up to  $0.1^{\circ}\text{C}$  can be read. At this time, care should be taken to check if stabilized condition is realized.

8. Even though there is a difference between the temperature of the Still section and of the top section, do not care anything for it.

The most important thing in this experiment is that a temperature rise of both vapor and liquid at the Cottrell pump section is essential. This features an excellent point which distinguishes this system from others.

9. Process of operation (See the drawing No.3)

Generated vapor is cooled and liquidized in the condensing column through the liquid distribution section and it returns to the liquid distribution section. It is necessary to control a dropping speed or interval of droplet from the end of the condensing column at a speed of approximately two second per one droplet.

10. An experiment operating duration time will be approximately 40 - 60 minutes (It may vary depending on each sample).

11. A small amount of mixed liquid being jetted is to be collected by opening the cock (B) of the section (9) in the drawing No.3. Further, vaporized liquid is collected by opening the cock (C).

Heating Method : How to heat up at the same time both vapor and liquid in the Cottrell pump is to master in a short period of time hoe to get used to operating it.

Finally, extracted sample liquid is evaluated by the analyzer.

HOW TO OPERATE the Vacuum/Pressure Reducing Exhaust System

(See the drawing No.1)

First, insert the electrical power supply cord to the measure operation section (20) in the drawing No.1.

Turn ON the power switch (6), and it will light.

When wishing to turn off, push again the power switch (6), and it will go out.

Set the Pirani Pressure gauge (2) to desired vacuum degree by using its setting knob.

(Appendix 6.2)

Push the vacuum control switch button (4).

Open the main flow rate control valve (8).

Note : Since this valve is a needle type valve, it requires many times of handle turning operation. It is recommended that a flow rate is properly controlled depending on the vacuum degree you want.

The leak valve (7) is to be shutoff.

Press the vacuum control switch button (4). This will make start a pressure reducing operation in the main experimental equipment. The pump will stop operating after it has reached a present vacuum level.

Further, when the vacuum degree rises above a preset vacuum level, the pump will start again operating to hold an appropriate vacuum degree.

#### Description of Attachment

The air cleaning column (9) is designed in such a manner that the flow tube is provided at a height of 4 - 5 cm where the air circulates inside the flow tube and is cleaned.

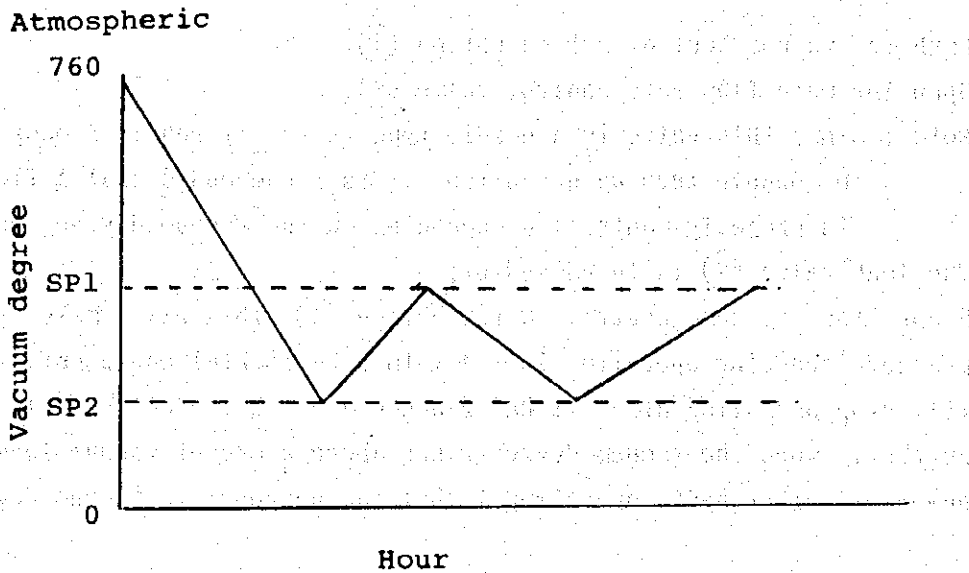
Activated charcoal is charged into the air dry column (10) in order to absorb water/humidity in the air.

Ice or dry ice is put in the Dewar flask (13) in order to collect the gas in the air. This is for the purpose of maintaining the safety in vacuum pump operation.

#### 4.0 Vacuum Control Method

1. Two contact points are established by SP1 and SP2, and the vacuum adjustment is controlled in the ON position as shown below.

(Appendix 6.2)



The SP1 corresponds to the low vacuum side and the SP2 corresponds to the side of high vacuum.

2. If it is controlled by Torr, for example, setting is done in such a figure as listed below.

SP1 -----  $2.2 \times 10^1$  Torr  
SP2 -----  $1.8 \times 10^1$  Torr

3. For further detail of the operation of key, see the description of Item 6.0 of this operation manual.

First, press the **FUN** key to flash and output the SP1 by the **▼** key.

Then, press the **ENT** key. A setting of vacuum degree is done using the **▼**, **▲** and **◀** key.

Memorize it by using the **ENT** key.

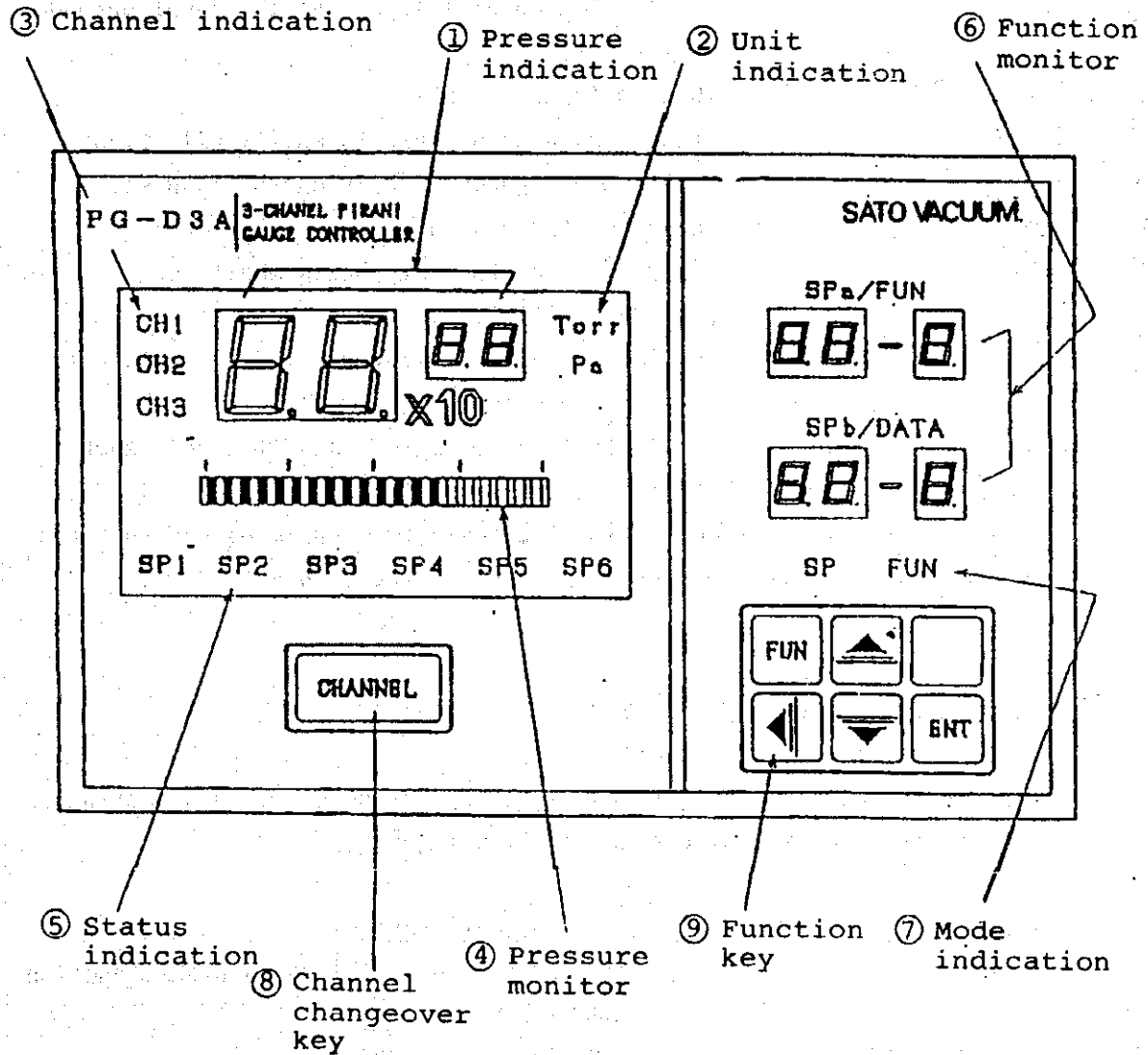
Next, output the SP2 by the **▼** key and memorize it in the same way. And return it using the **FUN** key.



(Appendix 6.2)

5.0 Description and Function of Each Section

5.1 Front Panel












(Appendix 6.2)

6.0 SP1 :

Setting Operation of 'SET POINT 1'

Set point 1 is used to set the required output pressure. This setting is effective only for measured pressure of CH1 gauge.

	<u>Key Operation</u>	<u>Description</u>
①		The 'FUN' lamp will light and the function mode will start.
②	 	This is to set to SP1.
③		Figures data to be able to modify will flash.
④	 	Modify the figures data which is flashing.
⑤		Shift the figures to modify.
⑥		Registering of the data being modified (the data will light).
⑦		The 'SP' lamp will light and it will return to the SP indication mode.









Note: A setting range is from  $0.0 \times 10^{-1}$  to  $9.9 \times 10^{-9}$  and if a real number is set to '0.0', then, Set point will not activate.

The setting point is effective for the indication valve of pressure and therefore, in the event of modifying the setting point.

SP2 :

Setting Operation of 'SET POINT 2'

The pressure data to be outputted is set by Set point 2. This setting is effective only for measured pressure of CH1 gauge.

	<u>Key Operation</u>	<u>Description</u>
①		The 'FUN' lamp will light and the function mode will start.
②	 	This is set to SP2.
③		Figures data to be able to modify will flash.
④	 	Modify the figures data which is flashing.
⑤		Shift the figures to modify.
⑥		Registering of the data being modified (The data will light.)

(Appendix 6.2)

7

**FUN**

The 'SP' lamp will light and it will return to the SP indication mode.

Note: A setting range is from  $0.0 \times 10^{-0}$  to  $9.9 \times 10^{-9}$  and if a real number is set to '0.0', then, Set point will not activate.

Function of Each Section

1. Pressure Indication:

The pressure measured value and error code are indicated. The pressure of CH1 is indicated with initial condition.

Larger indication shows a real number of pressure value and small one shows a exponent number.

When the channel not registered is indicated, the F will be displayed.

2. Channel Indication:

DCG - This will light in case of Discharge ON (during pressure measurement operation).

3. Pressure Monitor:

Pressure values are displayed in the analog manner of a bar graph of twenty elements. Since each range is a full-scale, one element will change every time 0.5 of a real number of pressure value will changes.

4. Status Indication

SP1 - This will light when the pressure value is below Set point one. A setting of Set point one is done using Function.

SP2 - This will light when the pressure value is below Set point two. A setting of Set point two can be done using Function.

EXT - This will light when Discharge ON/OFF is in the external control mode.

Changeover of the external/internal can be done using the external input/output connector on the rear panel.

5. Function Monitor

SP1/FUN - The setting value of Set point one or the Function item are indicated.

SP2/DATA - The setting value of Set point two or the setting value of

(Appendix 6.2)

Function are indicated.

6. Mode Indication






- SP - This will light when it is in the set point indication mode. In this case, the function monitor displays the setting value of Set point one and two.
- FUN - This will light in case of the Function indication/setting mode. In this case, the function monitor displays the Function item and setting value.

7. Channel Changeover Key

Channel - This is used to changeover the channel which indicates the pressure.

The pressure indication will change in such a manner as CH1-- CH2 -- CH3 -- , every time this key is pressed. Further, the indication of Set point will also change the same time.

8. Function Key

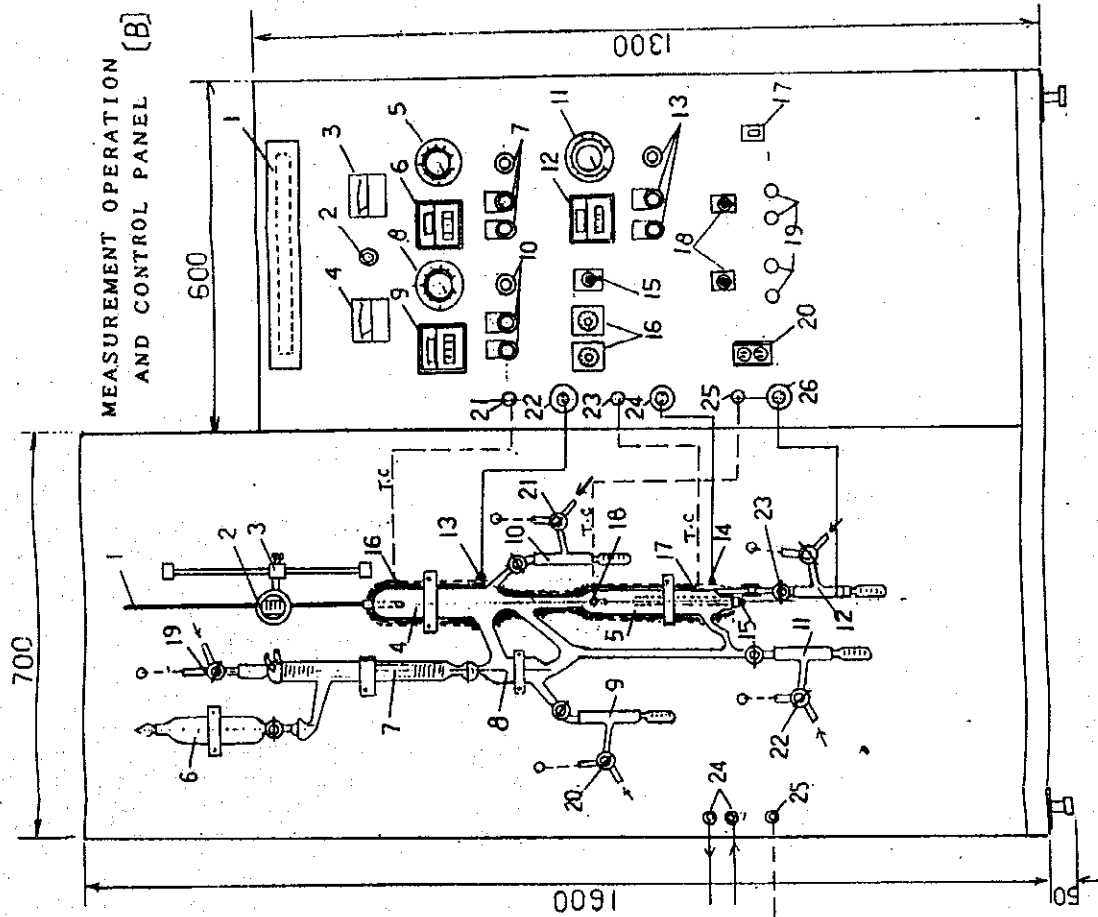
-  - This is used to switch the Set point indication mode and Function indication/setting mode.
-  - This is used to up-count the setting value or to select the Function item.
-  - This is a key to down-count the setting value or to select the Function item.
-  - This is a key to specify a number of figures of the setting value to be changed.
-  - This is used to determine the Function setting item or to register the setting value.

9. Measurement ON/OFF Key

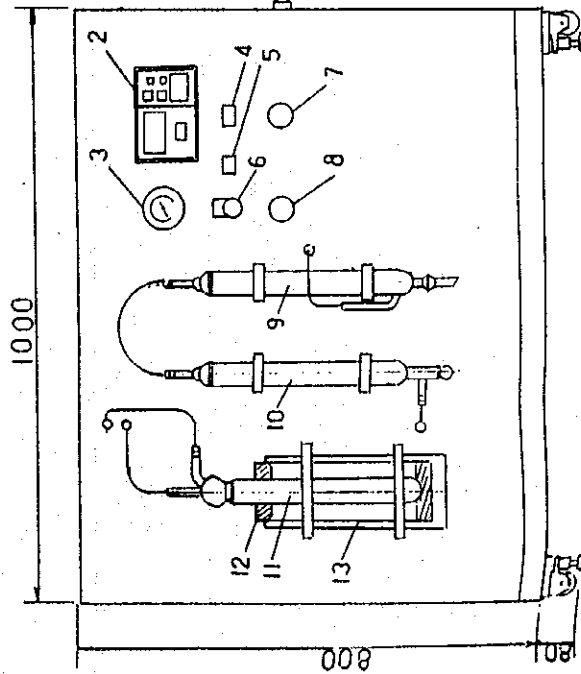
- DCG - This is used to perform ON/OFF of Discharge (Pressure measurement). In case of the external mode, it is impossible to operate this key.

VAPOR-LIQUID EQUILIBRIUM APPARATUS  
 MODEL M. R. W. (IMPROVED)

EQUILIBRIUM MAIN EQUIPMENT OF  
 THE EXPERIMENTAL APPARATUS [A]



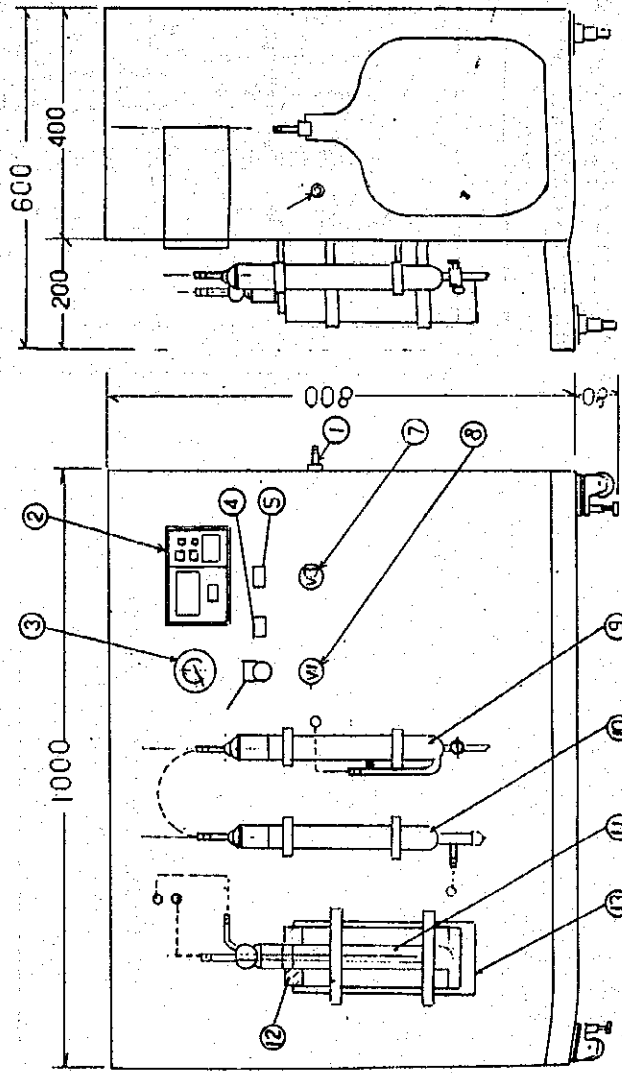
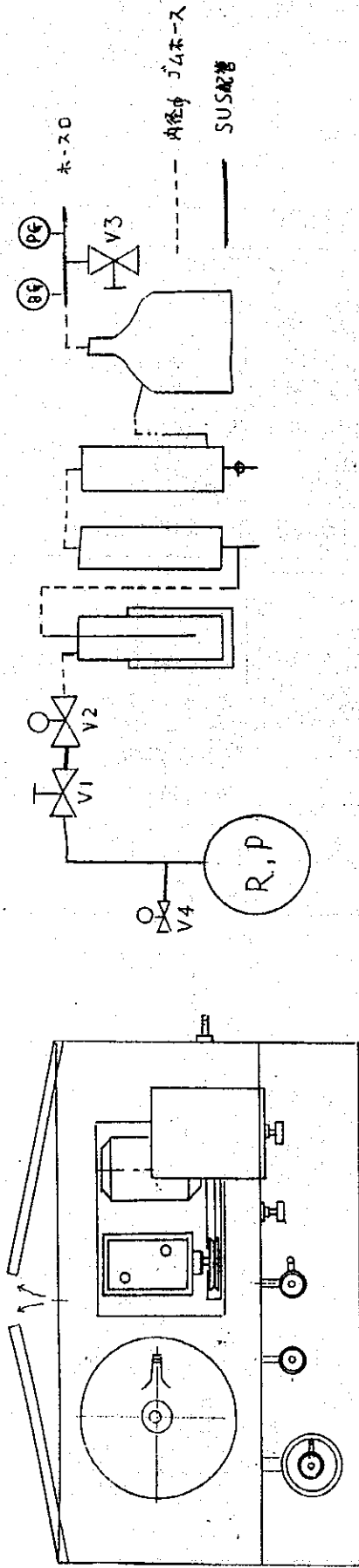
VACUUM/PRESSURE REDUCING  
 EXHAUST SYSTEM [C]



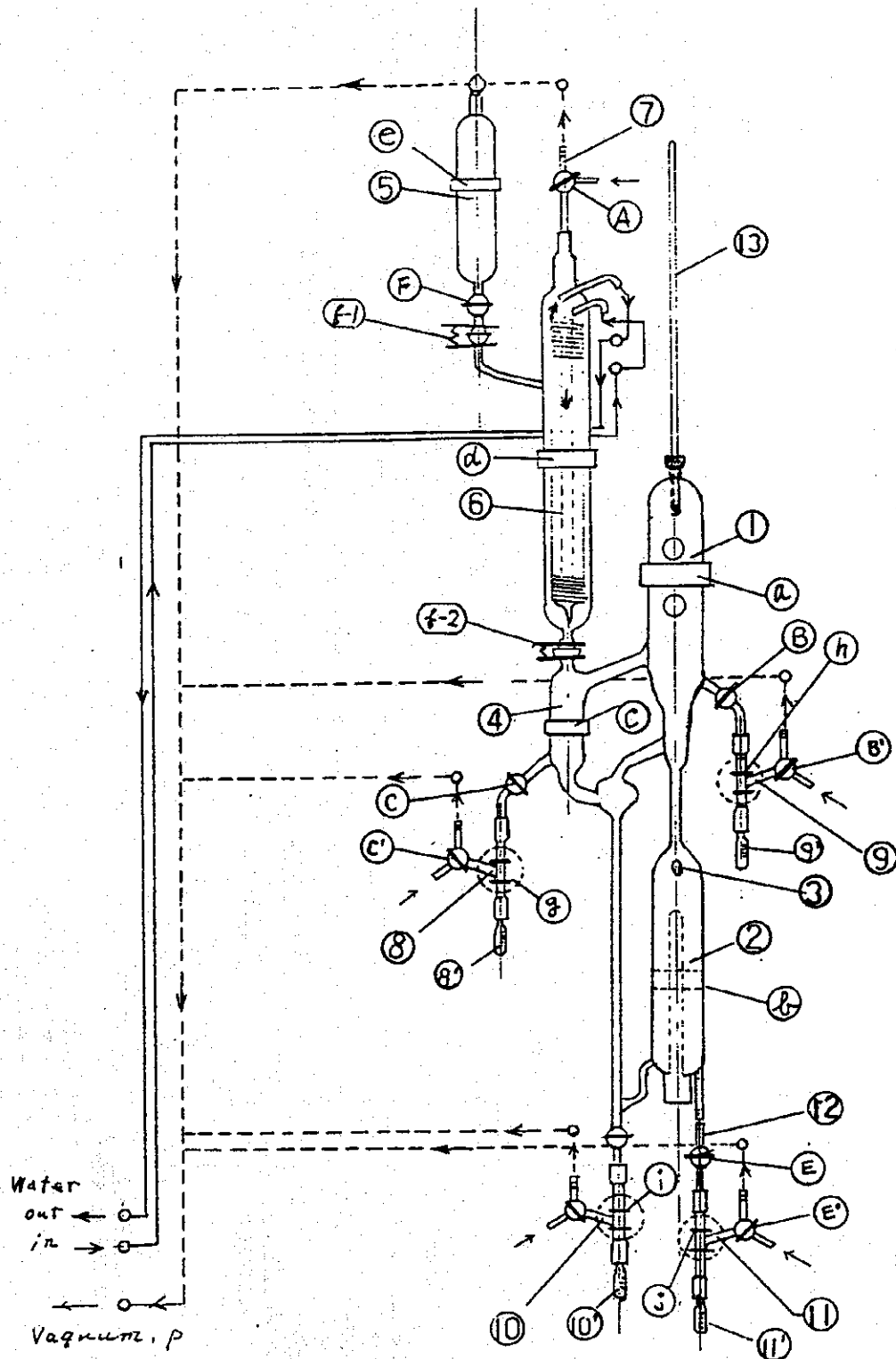
KYOWA INTERFACE SCIENCE CO., LTD.

VACUUM/PRESSURE REDUCING EXHAUST SYSTEM

SYSTEM STRUCTURE



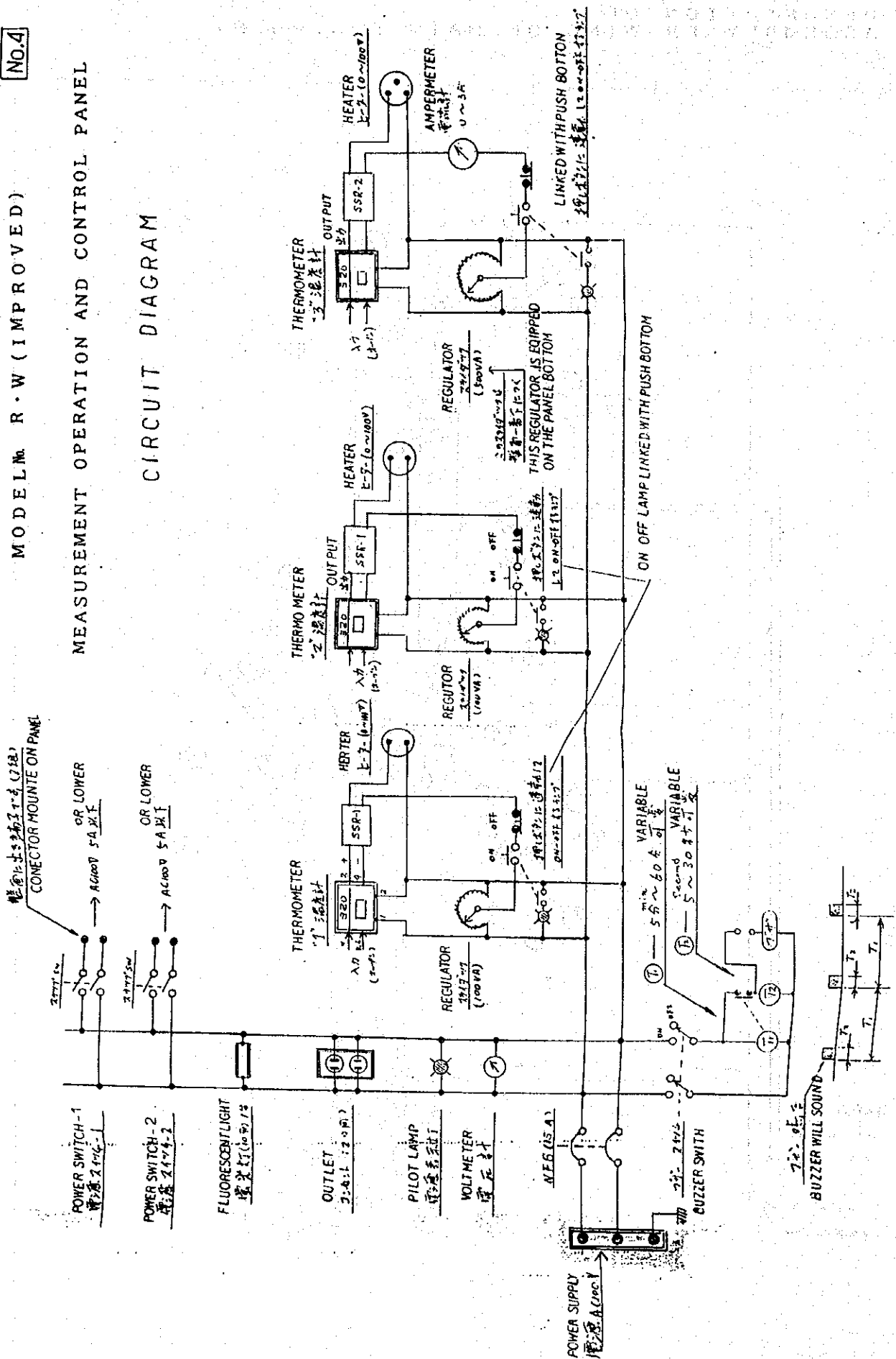
DESCRIPTION OF  
ASSEMBLY DRAWING OF MAIN EQUIPMENT



KYOUWA INTERFACE SCIENCE CO., LTD.

VAPOR-LIQUID EQUILIBRIUM APPARATUS  
 MODEL No. R.W (IMPROVED)  
 No.4

MEASUREMENT OPERATION AND CONTROL PANEL  
 CIRCUIT DIAGRAM



KYOWA INTERFACE SCIENCE CO., LTD.



DRAWING No.1 : ASSEMBLY DRAWING OF MAIN EQUIPMENT

- ① Equilibrium Main Equipment, Upper Section
- ② Equilibrium Main Equipment, Still Section
- ③ Insert port for Still Heater Sensor
- ④ Liquid Distribution Section
- ⑤ Sample Charging Column
- ⑥ Vapor Condensing Column
- ⑦ Vacuum/Atmospheric Changeover Unit, Upper Section
- ⑧ No.1 Changeover Cock and Sample Collecting Column
- 8' Sample Collecting Column
- ⑨ No.2 Changeover Cock and Sample Collecting Column
- 9' Sample Collecting Column
- ⑩ No.3 Changeover Cock and Sample Collecting Column
- 10' Sample Collecting Column
- ⑪ No.4 Changeover Cock and Sample Collecting Column
- 11' Sample Collecting Column
- ⑫ Still Takeout Cock
- ⑬ Thermometer
- ① Main Equipment Upper Section Fixing Fitting
- ② Still Section Fixing Fitting
- ③ Liquid Distribution Section Fixing Fitting
- ④ Vapor Condensing Column Fixing Fitting
- ⑤ Sample Charging Column Fixing Fitting
- f-1 Ball Joint Nipper
- f-2 Ball Joint Nipper
- A-F Changeover Glass Cock
- B'-D'

