approaching that of $NaIO_3$ but is exceeding it by a larger amount than in more dilute solutions.

The behavior of *p*-toluenesulfonic acid and sodium *p*-toluenesulfonate resembled more closely that of HCl and NaCl, but in the more concentrated solutions there is evidence of incomplete ionization of the acid. The difference in partial molal volumes of the acids and corresponding salts at 4.0*m* is 2.1 ml for the chlorides but only 1.4 ml for the toluenesulfonates. A degree of ionization of 0.94 has been calculated of *p*-toluenesulfonic acid at 4.0*m*.

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Apparatus for Measurement of Isobaric Dew and Bubble Points and Vapor-Liquid Equilibria

Methanol-Water and Water-Dioxane Systems

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A new apparatus for measurement of isobaric dew and bubble points and vapor-liquid equilibria makes it possible to measure dew and bubble points of any given composition without analysis. Vapor-liquid equilibrium relations may be measured at any vapor or liquid composition appointed and the apparatus can be applied to the usual Othmer-type measurements. With the apparatus, vapor-liquid equilibrium relations were determined at atmospheric pressure for methanol-water and water-dioxane systems.

Vapor-liquid equilibrium relations are important properties of liquid mixtures, and isobaric data in particular are required for practical use, such as in the design and operation of distillation equipment.

For measurements of isobaric vapor-liquid equilibria, several types of apparatus have been proposed by Othmer and other investigators (*1*, *5*, *10*). In these conventional apparatus, it is necessary to analyze the sample and it is difficult to measure the vapor-liquid equilibrium relation at the exact point desired.

For measurements of isobaric dew points, a unique apparatus was proposed by Kojima *et al.* (*7*). In the apparatus, it is necessary to analyze the sample and it is difficult to measure the dew point at the precise composition desired. Furthermore, the bubble points must be determined by separate measurements or by theoretical estimations.

For measurement of isobaric bubble points, Cottrell (*2*), Kojima *et al.* (*6*, *8*), and Swietoslawski (*15*) have proposed some ebulliometers. However, in the general batch-type ebulliometer, it is necessary to correct for the difference between the liquid composition at steady state and the feed composition. The dew points must be determined separately.

The authors (*4*) previously proposed flow-type apparatus for measurement of isobaric dew and bubble points. However, it is not easy to measure dew and bubble points at the accurate composition desired, and for a multicomponent system this apparatus seems complex, because it is necessary to set each boiler for each component in the system studied.

In the present paper, a new apparatus for measurement of isobaric dew and bubble points and vapor-liquid equilibria is proposed, to eliminate as many disadvantages as possible.

EXPERIMENTAL APPARATUS

The apparatus for measurement of isobaric dew and bubble points and vapor-liquid equilibria is shown in Figure 1. It is constructed entirely of borosilicate glass. Its main parts are a dew point still, *D*, a bubble point still, *B*, three overflow tubes, *O*, a connecting tube, *C*, and a feeder, *F*.

The vapor from *D* does not return to that still but enters *B* after condensation. The internal construction of both stills is almost similar to that of the flow-type ebulliometer (*4*). Heat is supplied by Nichrome wires and a little glass dust is put on the wall of the heat transfer surface to stabilize boiling. The boiling vapor-liquid mixture rises through the Cottrell tube and flushes to the thermometer well. The amount of liquid contained in each still is about 15 cc; both stills are kept adiabatic with evacuated jackets and asbestos tapes. Using capillary connecting tube *C*, the liquid flows from *B* to *D*, as shown in Figure 1. Feeder *F* is 150 cc in volume and constructed like a general separating funnel.

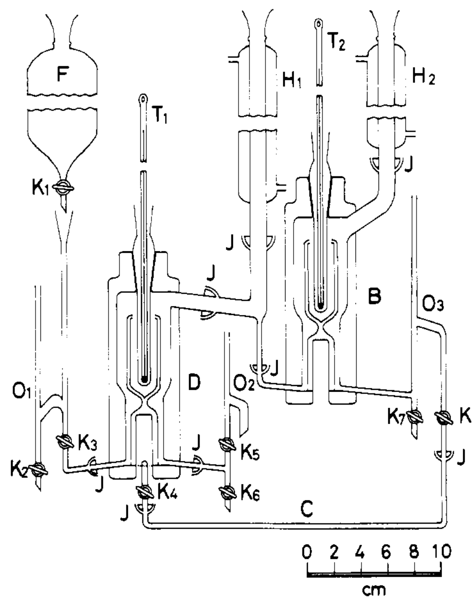

Figure 1. Experimental apparatus

B.	Bubble point still	*J.*	Ball joint
C.	Connecting tube	*K.*	Cock
D.	Dew point still	*O.*	Overflow tube
F.	Feeder	*T.*	Thermometer
H.	Condenser		

The experimental temperatures were measured with mercury thermometers, calibrated to ±0.1° C in accordance to the standard platinum resistance thermometer in the Swietoslawski ebulliometer (*15*). The standard thermometer was calibrated in the National Research Laboratory of Metrology, Japan, according to the specifications of the international practical temperature scale (*14*).

EXPERIMENTAL PROCEDURE

With the apparatus described, it is possible to measure dew and bubble points and vapor-liquid equilibria by several methods.

Method 1. Measurement of Dew and Bubble Points at Any Desired Composition without Analysis. At the start of the experiments, connecting tube *C* is taken off. Cocks K_2, K_3, and K_8 are opened, and cocks K_4, K_5, K_6, and K_7 are closed. A prepared solution of the given composition is charged from feeder *F* continuously and the flow rate can be controlled with cock K_1. The liquid is boiled in the dew point still, *D*, and the bubble point still, *B*. During the experiment, the feed partially overflows through the branched tube, O_1. After steady state has been attained, temperatures in stills *D* and *B* are measured.

The flow diagram is schematically shown in Figure 2. The composition of the overflowed liquid, x_S, equals the feed composition x_F as the feed partially overflows

$$x_S = x_F \tag{1}$$

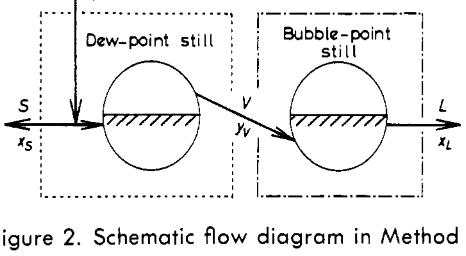

Figure 2. Schematic flow diagram in Method 1

The only material entering the region bounded by the dashed line in Figure 2 is the feed, *F*, while leaving the section is the partially overflowing liquid, *S*, and the vapor from the dew point still, *V*.

By mass balance,

$$F = V + S \tag{2}$$

$$Fx_F = Vy_V + Sx_S \tag{3}$$

where y_V represents the composition of the vapor obtained from the dew point still.

Substituting Equation 1 into Equation 3, and combining with Equation 2, gives

$$y_V = x_F \tag{4}$$

Likewise, making a mass balance on the bubble point still,

$$V = L \tag{5}$$

$$Vy_V = Lx_L \tag{6}$$

Substituting Equation 4 into Equation 6, and combining with Equation 5, give

$$x_L = y_V = x_F \tag{7}$$

Thus, the vapor composition in the dew point still and the liquid composition in the bubble point still must agree with the feed composition at steady state. Therefore, the temperatures obtained in stills *D* and *B* should equal the dew point and bubble point at the feed compositions, respectively. When based on the dew and bubble point method, the binary vapor-liquid equilibrium relations may be determined without analysis using this procedure.

Method 2. Measurement of Vapor-Liquid Equilibrium Relations at Any Vapor Composition. The procedure is almost identical to that in Method 1. But after steady state has been attained, the liquid in still *D* is taken out for analysis through cock K_4 or K_6. Considering mass balance, the liquid composition in the dew point still should agree with the liquid composition, which is in equilibrium with the vapor of the feed composition at steady state.

Method 3. Measurement of Vapor-Liquid Equilibrium Relations at Any Liquid Composition. First, capillary tube *C* is attached. Cocks K_3, K_4, K_5, and K_8 are opened and cocks K_2, K_6, and K_7 are closed. The prepared solution of given composition is charged continuously from feeder *F*, and the liquid is boiled in both stills. In this experiment, the liquid in dew point still *D* overflows through branched tube O_2. After steady state has been attained, the liquid in bubble point still *B* is taken out for analysis through cock K_7. Based on mass balance, the liquid composition in the dew point still must agree with the feed composition. As a result, the liquid composition in bubble point still *B* equals the vapor composition, which is in equilibrium with the liquid of the feed composition.

Method 4. Usual Othmer-Type Measurements of Vapor-Liquid Equilibria. At the beginning of the experiment, connecting tube *C* is set. Cocks K_4 and K_8 are opened and cocks K_3, K_5, K_6 and K_7 are closed. The liquid mixture is charged to stills *D* and *B*, and is boiled in each still. After steady state has been attained, both liquids in the still are taken out for analysis. At steady state, the liquid compositions in the dew point and bubble point stills, respectively, should agree with the equilibrium liquid and vapor compositions at the temperature registered in the dew point still.

In the present investigation, the solution of desired composition was prepared by mixing each pure substance, which was accurately weighed within ±1 mg by use of an automatic balance. The steady state was certified by checking the movements of both temperatures in the stills. The period required for attainment of steady state lay between 15 and 45 minutes.

Table I. Physical Properties of Materials

Material	Density at 25° C, G/Cm³		Refractive Index at 25° C		Boiling Point, ° C	
	Obtained	Reported (*16*)	Obtained	Reported (*16*)	Obtained	Reported (*16*)
Methanol	0.7866	0.7865	1.3266	. . .	64.59	64.65
Dioxane	1.0279	1.0280	1.4201	1.4202	101.12	101.32

Table II. Experimental Data for Methanol-Water System at 760 mm of Hg by Methods 1 to 4

Method 1

No.	Methanol, Mole Fraction	Dew Point, ° C	Bubble Point, ° C
1- 1	0.050[a]	98.6	92.1
1- 2	0.100[a]	97.0	87.2
1- 3	0.200[a]	94.5	81.3
1- 4	0.300[a]	91.1	78.0
1- 5	0.400[a]	88.5	75.1
1- 6	0.500[a]	85.0	72.7
1- 7	0.600[a]	81.0	71.0
1- 8	0.700[a]	76.4	69.1
1- 9	0.800[a]	72.1	67.4
1-10	0.900[a]	68.2	66.0

Methods 2 to 4

No.	Methanol, Mole Fraction		Equilibrium Temp., ° C	Bubble Point of Vapor, ° C
	Liquid	Vapor		
2- 1	0.019	0.150[a]	96.0	83.7
2- 2	0.175	0.550[a]	82.8	71.9
2- 3	0.657	0.850[a]	70.2	66.8
3- 1	0.250[a]	0.624	79.8	70.7
3- 2	0.350[a]	0.696	76.8	69.4
3- 3	0.450[a]	0.764	74.2	68.3
4- 1	0.033	0.222	94.0	80.3
4- 2	0.076	0.381	89.3	75.8
4- 3	0.128	0.496	85.1	73.0

[a] Charge composition.

Table III. Experimental Data for Water-Dioxane System at 760 mm of Hg by Method 1

No.	Water, Mole Fraction[a]	Dew Point, ° C	Bubble Point, ° C
1	0.050	99.8	96.8
2	0.100	98.4	92.8
3	0.200	95.6	89.6
4	0.300	92.3	88.3
5	0.400	88.9	87.7
6	0.450	87.9	87.6
7	0.500	87.7	87.5
8	0.550	88.0	87.6
9	0.600	88.8	87.7
10	0.700	91.0	87.9
11	0.800	93.9	88.4
12	0.900	97.2	90.3
13	0.950	98.6	92.8

[a] Charge composition.

Table IV. Smoothed Data for Methanol-Water System at 760 mm of Hg by Isobaric Dew and Bubble Point Method (Method 1)

Methanol, Mole Fraction		Temp., ° C	Activity Coefficient		*Q*-Function
Liquid	Vapor		Methanol	Water	
0.030	0.174	95.0	1.956	1.021	0.040
0.068	0.342	90.0	1.999	1.020	0.066
0.129	0.498	85.0	1.818	1.010	0.086
0.237	0.620	80.0	1.467	1.066	0.139
0.365	0.710	76.0	1.260	1.151	0.174
0.445	0.754	74.0	1.181	1.215	0.182
0.540	0.802	72.0	1.115	1.285	0.174
0.647	0.852	70.0	1.066	1.364	0.151
0.769	0.905	68.0	1.028	1.459	0.108
0.900	0.960	66.0	1.006	1.551	0.050

Table V. Smoothed Data for Water-Dioxane System at 760 Mm of Hg by Isobaric Dew and Bubble Point Method (Method 1)

Water, Mole Fraction		Temp., ° C	Activity Coefficient		*Q*-Function
Liquid	Vapor		Water	Dioxane	
0.019	0.079	99.0	4.310	1.005	0.033
0.047	0.186	96.0	4.573	1.005	0.076
0.077	0.250	94.0	4.038	1.019	0.125
0.119	0.309	92.0	3.480	1.005	0.191
0.183	0.366	90.0	2.891	1.109	0.279
0.226	0.396	89.0	2.631	1.152	0.328
0.261	0.418	88.5	2.451	1.182	0.358
0.325	0.450	88.0	2.160	1.244	0.397
0.416	0.485	87.7	1.840	1.359	0.433
0.510	0.510	87.6	1.584	1.547	0.448
0.600	0.525	87.7	1.381	1.831	0.436
0.731	0.550	88.0	1.174	2.553	0.369
0.845	0.611	89.0	1.086	3.706	0.272
0.890	0.659	90.0	1.070	4.429	0.224
0.938	0.736	92.0	1.052	5.699	0.155
0.965	0.803	94.0	1.035	7.062	0.102
0.980	0.861	96.0	1.015	8.180	0.057
0.991	0.928	98.0	1.006	8.838	0.026

Table VI. Wilson Parameters for Two Binary Systems at 760 Mm of Hg Pressure

System	Λ_{12}	Λ_{21}
Methanol (1)-water (2)	0.37221	1.05311
Water (1)-dioxane(2)	0.36230	0.17260

MATERIALS

Reagents supplied by the Showa Chemical Co., Ltd., were used without further purification. The physical properties of the reagents used are listed in Table I.

EXPERIMENTAL RESULTS

To confirm the reliability of the present apparatus and experimental methods, the experiments were made first by measuring the vapor-liquid equilibrium relations for the methanol-water system at atmospheric pressure, whose equilibrium relations were already determined precisely in the literature. All the methods mentioned above were used and tested in the experiments. After the experiments for the methanol-water system, the vapor-liquid equilibrium relations were measured by Method 1, without analysis, for the water-dioxane system at atmospheric pressure. Large differences were observed among data in the literature (*9, 12, 13*).

The experimental data obtained are presented in Tables II and III. The experimental temperatures were corrected to the values at 760 mm of Hg pressure, by measuring the boiling points of water in the Swietoslawski ebulliometer (*15*) with the platinum resistance thermometer previously

Table VII. Root Mean Squares Deviations in Vapor Composition Using Wilson Parameters Listed in Table VI

Methanol-Water System: Data	δy	Water-Dioxane System: Data	δy
Our data by Method 1	0.0107	Our data by Method 1	0.0238
Our data by Methods 2 to 4	0.0075	Komatsu *et al.* (*9*)	0.0335
Othmer and Benati (*10*)	0.0100	Schneider and Lynch (*12*)	0.0338
Uchida and Kato (*17*)	0.0136	Smith and Wojielchowski (*13*)	0.0647

δy. Root mean squares deviation in vapor mole fraction.

mentioned. In the experiments of Methods 2 to 4, the samples were analyzed by gas chromatography.

The smoothed values measured by Method 1 are listed in Tables IV and V. The individual activity coefficient and Q-function were calculated by the following equations, assuming that the vapor phase imperfection could be ignored:

$$\gamma_1 = \frac{\pi y_1}{P_1 x_1}, \quad \gamma_2 = \frac{\pi y_2}{P_2 x_2} \tag{8}$$

$$Q = x_1 \log \gamma_1 + x_2 \log \gamma_2 \tag{9}$$

The vapor pressures for methanol (*6*), water (*6*), and dioxane (*9*) were obtained from the literature. The thermodynamic consistency of the equilibrium data was first checked by the Herington area test (*3*). The positive and negative areas of the plots for the systems methanol-water and water-dioxane agree within 0.8 and 5.4%, respectively, indicating the thermodynamic consistency of the equilibrium data. The equilibrium data listed in Tables IV and V were then correlated with the Wilson equation (*18*):

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12} x_2) + x_2 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right) \tag{10}$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21} x_1) - x_1 \left(\frac{\Lambda_{12}}{x_1 + \Lambda_{12} x_2} - \frac{\Lambda_{21}}{\Lambda_{21} x_1 + x_2} \right) \tag{11}$$

Values of parameters Λ_{12} and Λ_{21} were determined to minimize the sum of squares of deviations in Q-values for all data points using a digital computer. The Wilson parameters obtained are listed in Table VI. The root mean square deviations of Q-values were 0.0067 for the methanol-water system and 0.0123 for the water-dioxane system. As shown in Table VII, the calculated vapor compositions were compared with the experimental and literature values using the Wilson parameters listed in Table VI. In the experiments for the methanol-water system, our data obtained by all the methods agreed well with previous data (*10, 17*), confirming the reliability of the present apparatus and experimental methods. For the water-dioxane system, the previous data (*9*) measured in our laboratory agreed fairly well with the present data.

The authors are planning to make an improved apparatus by adding a flow-type ebulliometer (*4*) to the present apparatus, as shown in Figure 3. The procedure is almost identical to that of the present apparatus. In the experiments of Methods 1 and 2, the temperature in ebulliometer *E* should agree with that in still *B* at steady state. In the case of Method 3, the temperature difference between ebulliometer *E* and still *D* must become zero at steady state. Therefore, when using the improved apparatus, the certification of steady state seems to be easier than in the present apparatus.

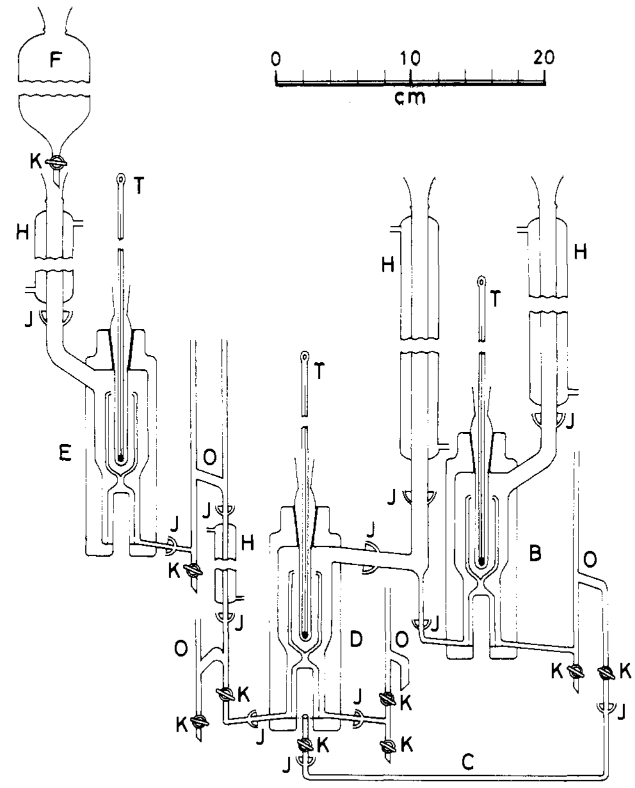

Figure 3. Improved apparatus

B. Bubble point still
C. Connecting tube
D. Dew point still
E. Flow-type ebulliometer
F. Feeder
H. Condenser
J. Ball joint
K. Cock
O. Overflow tube
T. Thermometer

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NOMENCLATURE

F = feed, grams per minute
L = liquid overflowed from bubble point still, grams per minute
P = vapor pressure, mm of Hg
Q = Q-function
S = partially overflowed liquid, grams per minute
V = vapor obtained from dew point still, grams per minute
x = liquid composition, mole fraction
x_F = feed composition, weight fraction
x_L = liquid composition of L, weight fraction
x_S = liquid composition of S, weight fraction
y = vapor composition, mole fraction
y_V = vapor composition of V, weight fraction

Greek Letters

γ = activity coefficient
δ = root mean squares deviation
Λ_{12}, Λ_{21} = Wilson parameters
π = pressure, mm. of Hg

Subscripts

1 = light component
2 = heavy component

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Enthalpy of Alkali Metal Fluoroborates from 298–1000° K

Enthalpies and Entropies of Fusion and Transition

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The enthalpies and entropies of $NaBF_4$, KBF_4, $RbBF_4$, and $CsBF_4$ have been measured from 298 to 1000° K with a copper block drop calorimeter. Their enthalpies of melting in kcal $mole^{-1}$ are 3.25, 4.30, 4.68, and 4.58, respectively, and enthalpies of transition are 1.61, 3.30, 2.86, and 1.94, respectively. The entropies of melting in cal deg^{-1} $mole^{-1}$ for the four salts are 4.78, 5.10, 5.5, and 5.5, respectively, while entropies of transition are 3.1, 5.9, 5.5, and 4.4, respectively. The transition behavior is discussed in terms of differences in structure and cation size.

Sodium fluoroborate is the main component of a proposed coolant mixture for a molten salt reactor. We have measured the high temperature enthalpies of $NaBF_4$, KBF_4, $RbBF_4$, and $CsBF_4$ to obtain information for reactor technology as well as to explore the interesting transition behavior of the solid fluoroborates. The melting points and solid transition temperatures, densities and molar volumes, and predicted volume changes on transition of the alkali fluoroborates have been reported (*3*). We now propose to examine the effect of the differences in structure and cation size on the enthalpy and entropy of fusion and transition in the alkali fluoroborates.

EXPERIMENTAL

The copper block drop calorimeter used for the measurements as well as the experimental procedure have been described in detail previously (*5*). Briefly, the experiment is performed by measuring the temperature rise of a copper block when an equilibrated encapsulated sample is dropped into a well in the block from the constant temperature zone of a controlled tube furnace. The enthalpy equivalent of the calorimeter relates the temperature rise of the block to the enthalpy of the sample and was determined with a NBS sample of synthetic sapphire using the same procedure as described above. The temperature of the sample was measured to ±0.1° with a calibrated platinum (90% platinum-10% rhodium) thermocouple. The temperature rise of the block was measured to ±0.001° with a calorimetric-type, platinum-sheathed platinum resistance thermometer. The salts were sealed in an inner platinum liner to prevent attack on the inconel capsules especially designed for our enthalpy apparatus. The enthalpy of the empty inconel capsules was measured in a separate series of experiments. The enthalpy of the platinum (*10*) amounted to only about 10 to 15% of that of the salt. Both the platinum and inconel capsules were welded closed in a helium drybox.

$NaBF_4$ and KBF_4 were prepared by recrystallization of commercial $NaBF_4$ and KBF_4 from dilute HF solutions. Further treatment of molten $NaBF_4$ at 425° C with a mixture of anhydrous HF, BF_3, and helium improved its purity. Sharp breaks in the DTA melting curves were obtained for $NaBF_4$ and KBF_4 at 406 and 569° C, respectively. $RbBF_4$ and $CsBF_4$ were prepared by the following reactions:

$$H_3BO_3(cr) + 4HF\ (58\%\ aq) = HBF_4(aq) + 3H_2O(l) \quad (1)$$

$$MF(aq) + HBF_4(aq) = MBF_4(cr) + HF(aq) \quad (2)$$