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Date: 8/6/08

**INVESTIGATION OF THE SYSTEM
METHYL ETHER AND METHYL BORATE-BORON FLUORIDE COMPLEX**

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INVESTIGATION OF THE SYSTEM
METHYL ETHER AND METHYL BORATE-BORON FLUORIDE COMPLEX

SUMMARY

It was observed in this laboratory that the separation of methyl borate-boron fluoride complex from dimethyl ether was much more difficult than would be expected from the vapor pressures of the two components. It was therefore postulated that the following equilibrium could exist:

In order to investigate this possibility, vapor pressures of the system methyl borate complex-methyl ether were measured over a wide composition range and at various temperatures.

The results not only verified the existence of the equilibrium but also provided data for the calculation of the equilibrium constant, the free energy change and the heat content change for the reaction.

INTRODUCTION

On a number of occasions it was observed in this laboratory that it was difficult to separate methyl borate-boron fluoride complex from methyl ether by distillation. This was surprising in view of the wide difference in volatilities of the two compounds as indicated in the following table:

	<u>Boiling Point at 1 atmosphere</u>	<u>Vapor Pressure at 25°C.</u>
Methyl Borate-Boron Fluoride Complex	87°C.	.13 mm.
Methyl Ether	-24°C.	4450 mm.

If mixtures of methyl borate complex and methyl ether followed Raoult's and Dalton's laws, the relative volatility would be the ratio of the vapor pressures or approximately 340. This would indicate that a fifty mole per cent mixture could be separated by a one-plate simple distillation into two batches containing approximately 98.5% of the ether and of the methyl borate complex, respectively. However, in the analysis of samples containing these components it was found that four or five plates were usually required for this degree of separation.

It was therefore postulated that a reaction between the methyl borate complex and the ether occurred as represented by the following equation:

Additional basis for postulating the occurrence of such a reaction was furnished by Sabi¹, who noticed the presence of methyl borate along with other decomposition products when methyl ether-boron fluoride complex was heated with water.

¹Sabi, SAM Report 4-1407, p. 6.

In order to test the validity of equation (1) and if possible to determine the equilibrium constants, the vapor pressures of methyl borate complex-methyl ether mixtures were measured over a wide range of temperature and composition.

APPARATUS

The vapor pressure measuring apparatus, shown diagrammatically in Figure 1, and photographed in Figure 2, consists of the following parts:

An oil bath maintained at a constant temperature within $\pm .05^{\circ}\text{C}$.

A vapor pressure bulb constructed from a 150 ml. round bottom flask fitted with a copper to glass seal and a brass valve.

A line of one-eighth inch copper tubing connecting the vapor pressure flask to the null manometer and the measuring manometer. This line was made of copper instead of glass to permit agitation of the flask.

A small null manometer, one side of which was connected to the vapor pressure flask and the other to the measuring manometer. The two sides of the null manometer were joined through a bypass line which was kept closed except when the apparatus was being evacuated. The manometer and the line leading to the flask were kept immersed in the bath liquid.

An open end measuring manometer upon which was read the pressure of the air introduced to balance the null manometer.

A three-way stopcock through which air could be added to or removed from the measuring manometer.

A transfer line, shown in Figure 3, was also set up for charging material to the vapor pressure bulb. This was equipped with proper connections to the vapor pressure bulb, to a cylinder of methyl ether, and to a receiver containing methyl borate-boron fluoride complex. Bulb "A" was also provided for condensation and redistillation of the methyl ether.

PROCEDURE FOR THE DETERMINATION OF VAPOR PRESSURE

The methyl borate complex used was obtained from the thermal decomposition products of the methyl ether-boron fluoride complex and purified by distillation through a ten-plate column. Its boiling point, 87°C ., and freezing point, 39°C ., agreed well with the accepted literature values, indicating a high degree of purity.

The methyl borate complex was introduced into the vapor pressure bulb by means of the transfer line shown in Figure 3. A receiver containing the distilled methyl borate complex was attached to this line and evacuated. The weighed vapor pressure bulb was then connected to the apparatus, cooled in liquid air and the methyl borate complex allowed to distill over. When enough complex had been collected the vapor pressure bulb was removed, weighed, and reconnected for the addition of methyl ether.

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~~SECRET~~

Figure 1

VAPOR PRESSURE
MEASURING APPARATUS~~SECRET~~D.A.M.
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7

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6

Figure 3
TRANSFER LINE

D.A.M.
6-7-45

The ether was allowed to distill from the cylinder into tube A, which was surrounded by a dry ice-trichloroethylene bath. About one-half of the ether collected in tube A was then distilled into the vapor pressure bulb, which was then removed and weighed. Only one-half of the ether was used in order to eliminate water, methanol or other impurities.

After the vapor pressure bulb was charged, it was attached to the vapor pressure measuring apparatus (Figure 1). The by-pass valve was opened and the system was evacuated. The by-pass valve was then closed and the valve to the bulb opened slowly while the null manometer was balanced carefully by bleeding air into the system. The oil bath was raised and brought to temperature. The flask was shaken and manometer balanced until the pressure became constant. The vapor pressure was read on the measuring manometer.

After a measurement was complete, the bath temperature was raised and the procedure repeated at a higher temperature. When all the desired readings had been obtained, the vapor pressure was checked again at a low temperature to see whether any irreversible decomposition had occurred. The vapor pressure bulb was then removed for the preparation of another mixture.

EXPERIMENTAL RESULTS

The experimental results are shown in Table I.

TABLE I

<u>Weight of Methyl Borate Complex</u>	<u>Weight of Dimethyl Ether</u>	<u>Mole Fraction of Dimethyl Ether</u>	<u>Temp. °C.</u>	<u>Vapor Pressure mm. of Hg</u>
82.4182 g.	11.0062 g.	0.411	0	50
"	"	"	30	216
"	"	"	40	321
"	"	"	50	466
"	22.2438 g.	0.584	0	105
"	"	"	30	366
"	"	"	40	516
"	"	"	50	746
50.4378	22.2909 g.	0.698	0	290
"	"	"	30	819
"	28.2150 g.	0.745	0	525

DETERMINATION OF THE EQUILIBRIUM CONSTANTS

1. Expression in Terms of Variables

The equilibrium constant, K, for reaction (1) is defined as:

$$K = \frac{[B(OMe)_3] [BF_3 \cdot Me_2O]^2}{[B(OMe)_3 \cdot 2BF_3] [Me_2O]^2} \quad (2)$$

The activities of methyl borate complex, methyl borate and methyl ether complex will be expressed as mole fractions, while the activity of methyl ether will be expressed as a partial pressure of gas in millimeters of mercury. This assumes that the liquid follows the perfect solution laws and that methyl ether vapor behaves as a perfect gas. Whether or not these assumptions are at least approximately valid will be shown by the results of the calculations. In other words, the vapor pressure measurements will be used to prove the validity of these assumptions as well as to prove the existence of the equilibrium. On this basis equation (1) may be expressed in terms of the following variables:

where, A = Moles of methyl borate-boron fluoride complex originally present
C = Moles of methyl ether added
b = Moles of ether reacted

case the p_{me} = Partial pressure of methyl ether in mm. of Hg, in which equilibrium constant is then expressed as:

$$K = \frac{\frac{\frac{b}{2}}{(A+C)} \cdot \frac{(\frac{b}{2})^2}{(A+C)^2}}{(p_{me})^2 \cdot \frac{A - \frac{b}{2}}{(A+C)}} = \frac{b^3}{2(p_{me})^2 (A+C)^2 (A - \frac{b}{2})} \quad (4)$$

2. Calculation of Partial Pressure of Ether and Moles of Ether Reacted

In order to calculate K, it is necessary to set up further relationships for determining b and p_{me} . These are supplied by the assumption that Raoult's law holds for this system. Thus,

$$p_{me} = P_{me} \frac{(c-b)}{(A+C)} \quad (5)$$

where, P_{me} = Vapor pressure of pure methyl ether at the temperature in question. c-b is used as the number of moles of unreacted ether in solution, since the amount of ether in the gas phase above the solution is

calculated to be less than one per cent of the total amount of unreacted ether, and may therefore be neglected. Also,

$$p_{mbc} = P_{mbc} \frac{b}{A + C} \quad (6)$$

$$p_{mb} = P_{mb} \frac{b}{2(A + C)} \quad (7)$$

$$p_{mec} = P_{mec} \frac{b}{A + C} \quad (8)$$

where, p_{mbc} = partial pressure of the methyl borate complex

P_{mbc} = Vapor pressure of pure methyl borate complex

p_{mb} = partial pressure of methyl borate

P_{mb} = Vapor pressure of pure methyl borate

p_{mec} = partial pressure of the methyl ether complex

P_{mec} = Vapor pressure of pure methyl ether complex

Then if Π = Total pressure, as measured in the vapor pressure apparatus,

$$\Pi = p_{me} + p_{mbc} + p_{mb} + p_{mec} \quad (9)$$

$$\text{or } p_{me} = \Pi - p_{mbc} - p_{mb} - p_{mec} \quad (10)$$

Substituting the values for p_{mbc} , p_{mb} , and p_{mec} from (6), (7) and (8),

$$p_{me} = \Pi - P_{mbc} \frac{b}{A + C} - P_{mb} \frac{b}{2(A + C)} - P_{mec} \frac{b}{A + C} \quad (11)$$

$$p_{me} = \Pi - P_{mbc} \frac{A}{A + C} - \frac{b}{A + C} \left[\frac{P_{mb} - P_{mbc}}{2} + P_{mec} \right] \quad (12)$$

By transposing equation (5), b may be expressed as,

$$b = C - \frac{p_{me}}{P_{me}} (A + C) \quad (13)$$

Substituting the value of b from (13) into equation (12),

$$p_{me} = \Pi - P_{mbc} \frac{A}{A + C} - \frac{C}{A + C} \left[\frac{P_{mb} - P_{mbc}}{2} + P_{mec} \right] + \frac{p_{me}}{P_{me}} \left[\frac{P_{mb} - P_{mbc}}{2} + P_{mec} \right] \quad (14)$$

$$\text{or } p_{\text{me}} = \frac{\Pi - P_{\text{mbc}} \frac{A}{A+C} - \frac{C}{A+C} \left[\frac{P_{\text{mb}} - P_{\text{mbc}}}{2} + P_{\text{mec}} \right]}{1 - \frac{1}{P_{\text{me}}} \left[\frac{P_{\text{mb}} - P_{\text{mbc}}}{2} + P_{\text{mec}} \right]} \quad (15)$$

Equation (15) above is the relationship used for calculating the partial pressure of methyl ether corresponding to a given total pressure. After the partial pressure of methyl ether is obtained, equation (13) is used for calculating b. In carrying out these calculations, the following values were used for the vapor pressures of the pure substances^{2,3}:

	0°	30°	40°	50°
Methyl Ether (P_{me})	1990 mm.	5140 mm.	6770 mm.	8590 mm.
Methyl Borate Complex (P_{mbc})	2 mm.	19 mm.	39 mm.	75 mm.
Methyl Borate (P_{mb})	36 mm.	158 mm.	240 mm.	350 mm.
Methyl Ether Complex (P_{mec})	0.5 mm.	5 mm.	10 mm.	18 mm.

The results of these calculations are shown in Table II.

TABLE II

Mole Fraction of Methyl Ether in Mixture	Temp. °C.	Total Pressure Π (mm)	P_{me} (mm)	b
.411	0	50	41	.2270
.584	0	105	94	.4440
.698	0	290	279	.3867
.745	0	525	515	.3997
.411	30	216	177	.2190
.584	30	366	319	.4317
.698	30	819	773	.3796
.411	40	321	257	.2169
.584	40	516	443	.4289
.411	50	466	365	.2143
.584	50	746	636	.4318

3. Calculation of Equilibrium Constants

From the above partial pressures of the ether and the values of b the equilibrium constants may be calculated by means of equation (4). These calculations were made and the results together with the average constant at each temperature are given in Table III.

²Cardoso and Bruno, Journal De Chimie Physique, 20, 350 (1923)

³SAM Report, A-2120.

TABLE III

Temperature °C.	Mole fraction Dimethyl Ether	K	Average
0	0.411	4.44×10^{-5}	0°C. = 5.0×10^{-5} *
0	0.584	5.94×10^{-5}	
0	0.698	4.50×10^{-5}	
0	0.745	1.68×10^{-5}	
30	0.411	2.17×10^{-6}	30°C. = 3.6×10^{-6}
30	0.584	4.06×10^{-6}	
30	0.698	4.62×10^{-6}	
40	0.411	9.05×10^{-7}	40°C. = 1.6×10^{-6}
40	0.584	22.7×10^{-7}	
50	0.411	4.59×10^{-7}	50°C. = 7.4×10^{-7}
50	0.584	10.19×10^{-7}	

An attempt was made to compare the magnitude of experimental errors and possible deviations from Raoult's law with deviations in calculated values of K and hence to obtain a weighted mean at each temperature. However, it was found the weighted average so obtained did not differ appreciably from the unweighted average and therefore the latter was chosen. It is this average that is shown above in Table III.

4. Graphical Representation of the Equilibrium

In order to illustrate graphically the close adherence of the experimental partial pressure of methyl ether to values predicted by equation (1), theoretical ether pressures for an assumed equilibrium constant were plotted against the composition and compared with the experimental ether pressures. This was carried out as follows:

1. Plots (Figures 4, 5, 6 and 7) were made of the partial pressure of methyl ether against the mole fraction of ether in the mixture for each temperature, using the data from Table II.

2. A set of equilibrium constants was then assumed, and the theoretical partial pressures of methyl ether were calculated over a range of composition by the method shown below.

*In determining this value the calculated constant at 0.745 mole fraction was neglected because it differed considerably from the other calculated constants. Figure 4 shows that at this concentration a small deviation from Raoult's law or a small experimental error would cause a relatively large change in the constant.

The value for p_{me} given in equation (5) is substituted in equation (4) giving,

$$K = \frac{b^3}{2(A - \frac{b}{2})(C - b)^2 \frac{P_{me}^2}{2}} \quad (16)$$

Rearranging,

$$b^3 \frac{(1 + K \frac{P_{me}^2}{2})}{K(\frac{P_{me}^2}{2})^2} - 2b^2(A + C) + b(4AC + C^2) - 2AC^2 = 0 \quad (17)$$

For a given temperature P_{me} is fixed and assuming appropriate values of K, A and C, b is determined by solving the cubic equation. It was found that Horner's method was most convenient for this solution. From the values of b so obtained, p_{me} is calculated by equation (5).

3. The resulting curves are superimposed upon Figures 4, 5, 6 and 7 where they can be compared with the experimental ether pressures.

CALCULATION OF THE FREE ENERGY AND HEAT CONTENT CHANGE

The standard free energy change over the temperature range from 0 to 50° was calculated for reaction (1) from the values of the equilibrium constant, using the following equation:

$$\Delta F_o = -2.303 RT \log (K \times \frac{1}{760})$$

The values obtained were:

0°	$\Delta F_o = -1825$
30°	$\Delta F_o = -440$
40°	$\Delta F_o = +50$
50°	$\Delta F_o = +545$

ΔF_o was plotted against the absolute temperature (Figure 8) and the plot was a straight line which could be expressed by:

$$\Delta F_o = -14,700 + 47.1T \quad (18)$$

$$\text{or } \log K = \frac{3210}{T} - \frac{11.2}{2.303} \quad 16.02 \quad (19)$$

From inspection of equation (18) it can be seen that:

$$\Delta H = -14.7 \text{ Kcal.}$$

DISCUSSION

The theoretical curves in Figures 4, 5, 6 and 7 are based on two assumptions, namely:

1. The laws of the perfect solution are valid.
2. Methyl ether reacts reversibly with methyl borate complex according to equation (1).

The actual and predicted vapor pressures are in very close agreement as is shown in Table IV. Column 4 shows the Raoult's law pressure that is ordinarily used as the norm in predicting the vapor pressure of a binary mixture. Column 6 shows that actually there is a large negative deviation from this norm. Column 5 shows the pressure predicted by the postulated equilibrium. The fact that the values in Columns 5 and 6 agree so well with each other is conclusive evidence that the equilibrium does exist. It also shows that the perfect solution laws are at least approximately obeyed.

TABLE IV

K	Temp. °C.	Mole fraction Ether = Nme	Pressure Ether Assuming no reaction $p_{me} = P_{me} N_{me}$	Pressure of Ether Assuming Equilibrium	Actual Pressure
5.0×10^{-5}	0	0.411	818 mm.	40	41
		0.584	1162	95	94
		0.698	1389	278	279
		0.745	1483	450	515
3.6×10^{-6}	30	0.411	2113	147	177
		0.584	3002	350	319
		0.698	3588	825	773
1.6×10^{-6}	40	0.411	2782	220	257
		0.584	3954	500	443
7.4×10^{-7}	50	0.411	3530	310	365
		0.584	5017	720	636

Table III shows that the maximum average deviation from the mean equilibrium constant for any temperature is approximately 40%. This corresponds to an uncertainty of ± 0.2 Kcal. in the determination of the standard free energy change which is sufficiently accurate for the present purpose, which is to prove the existence of the equilibrium.

CONCLUSIONS

1. The existence of the equilibrium postulated in equation (1) has been verified by vapor pressure measurements of the methyl borate complex-methyl ether system.
2. The equilibrium constant, free energy change, and heat constant change for the reaction (1) have been calculated from the vapor pressure measurements obtained.

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Partial Pressure of Dimethyl Ether (mm. of Hg)

Figure 4
Me₂O and B(OMe)₃-2BF₃
System at 0°C

$K = 0$

1.0

2.0

3.0

4.0

5.0

$K = \infty$

D.M.C.
1.45

Mole Fraction of Dimethyl Ether in Mixture

KEUFFEL & ESSER CO., N. Y., NO. 11-1141
MADE IN U.S.A.
Millimeter, 1 mm. line and 0.1 mm. lines
Major

20

Figure 5
Me₂O and B(OMe)₃·2BF₃
System at 30°C.

Partial Pressure of Dimethyl Ether (mm. of Hg.)

800

700

600

500

400

300

200

100

2215 18

Mole Fraction of Dimethyl Ether in Mixture

0.1

0.2

0.3

0.4

0.5

0.6

0.7

0.8

1.0×10^{-6}

2.0

3.0

4.0

5.0

$K = \infty$

19

DAME
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KEUFFEL & ESSER CO., N. Y. NO. 359-141
Millimeter, 5 mm. lines accepted, cm. lines heavy.
MADE IN U. S. A.

Partial Pressure of Dimethyl Ether (mm. of Hg.)

800

700

600

500

400

300

200

100

19

225

Figure 6
 Me_2O and $\text{B}(\text{OEt})_3 \cdot 2\text{BF}_3$
System at 40°C .

Mole Fraction of Dimethyl Ether in Mixture

Partial Pressure of Dimethyl Ether (Mm. of Hg.)

Mole Fraction of Dimethyl Ether in Mixture

2445 20

Figure 7
 Me_2O and $\text{B}(\text{OMe})_3 \cdot 2\text{BF}_3$
System at 50°C .

$K = 0$

4.0×10^{-7}

6.0×10^{-7}

8.0×10^{-7}

$K = \infty$

DAMC
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Mole Fraction of Dimethyl Ether in Mixture

NEUFELT & ESSER CO., N.Y., NO. 37-141
Millimeter, 2 mm. line, printed, cm. line heavy.

ΔF_0 in Kilogram Calories

27

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