Table VII. Heats of Combustion of Representative Pure Hydrocarbons

Hydrocarbon	B.P. (°C.) (9)	Q_p (Net) (9)	100 × Coefficient Eq. 11
Paraffin			
n-Heptane	98.4	19,157	19,089.2
2,2,4-Trimethylpentane	99.2	19,065	
3-Ethylpentane	93.5	19,155	
2,2-Dimethylhexane	106.8	19,055	
Naphthene			
Cyclohexane	80.7	18,676	
Methylcyclohexane	100.9	18,642	
cis-1,2-Dimethylcyclopentane	99.5	18,750	18,880
trans-1,2-Dimethylcyclopentane	91.9	18,724	
cis-1,3-Dimethylcyclopentane	91.9	18,729	
Olefins			
cis-2-Heptene	98.5	19,022	
trans-2-Heptene	98.0	19,004	17,673
cis-3-Heptene	95.8	19,022	
trans-3-Heptene	95.8	19,004	
2-Ethyl-1-pentene	94	18,997	
Aromatics			
Benzene	80.1	17,259	17,265
Toluene	110.6	17,424	

ponents, followed by a summation of the heats of combustion of the components is possible in principle, but beyond present experimental feasibility. The method described, of separating the gasoline into hydrocarbon types and estimating the heat of combustion of the fuel from the proportions of each type found, is within the capacity of most petroleum testing laboratories, and provides a better correlation than has been found for other easily measured physical properties. It is, however, subject to limitations on the fuels to which it can be applied in the same manner, as, for example, the estimation of heat of combustion from aniline-gravity product—that is, the coefficients of the equation used in the calculation may be expected to be sensitive to factors which vary from one fuel type to another, such as the boiling range and mean boiling point of the fuel and perhaps, outside of certain rather wide limits, the proportions of the hydrocarbon types present in the fuel.

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Liquid-Vapor Equilibria of the System Bromine Trifluoride-Bromine Pentafluoride

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The purpose of the present investigation was determination and correlation of the liquid-vapor equilibria data on the system bromine pentafluoride–bromine trifluoride. Bromine forms three halogen fluorides. Bromine monofluoride has been reported but never isolated. Bromine trifluoride is stable up to about 180°C. Bromine pentafluoride has been reported to be stable at several hundred degrees centigrade. Both bromine trifluoride and pentafluoride react violently with water and organic compounds. This reactivity makes necessary the use of specialized equipment. The vapor pressures of the two pure components as reported in this work are in general more accurate than those previously available. No previous data are available for the liquid-vapor equilibria of this particular system.

METHODS AND APPARATUS

Equilibrium Still. An all-metal Othmer still of the type used by Barber and Cady (*1*) was modified for this investigation. All-welded nickel construction was used because of the excellent corrosion resistance of nickel to bromine fluorides. A schematic diagram of the equilibrium still is shown in Figure 1. A loading port placed rather high up on the boiling chamber was used to charge the interhalogen into the still. As it was impossible to see the level of interhalogen in the nickel charging pot, the still was first evacuated and then sufficient time was allowed for all the interhalogen to flow into the still. For best operation, approximately 100 mm. of interhalogen of appropriate composition was charged. The still was recharged for each pair of data points.

The still was heated by asbestos-covered Nichrome wire on one side of a loop of $^3/_8$-inch nickel tubing attached to the bottom of the boiling chamber. This mixed the contents of the boiling chamber by thermal cycling. Mixing was further enhanced by bringing the vapor condensate back to the center of the heating loop rather than directly to the boiling chamber.

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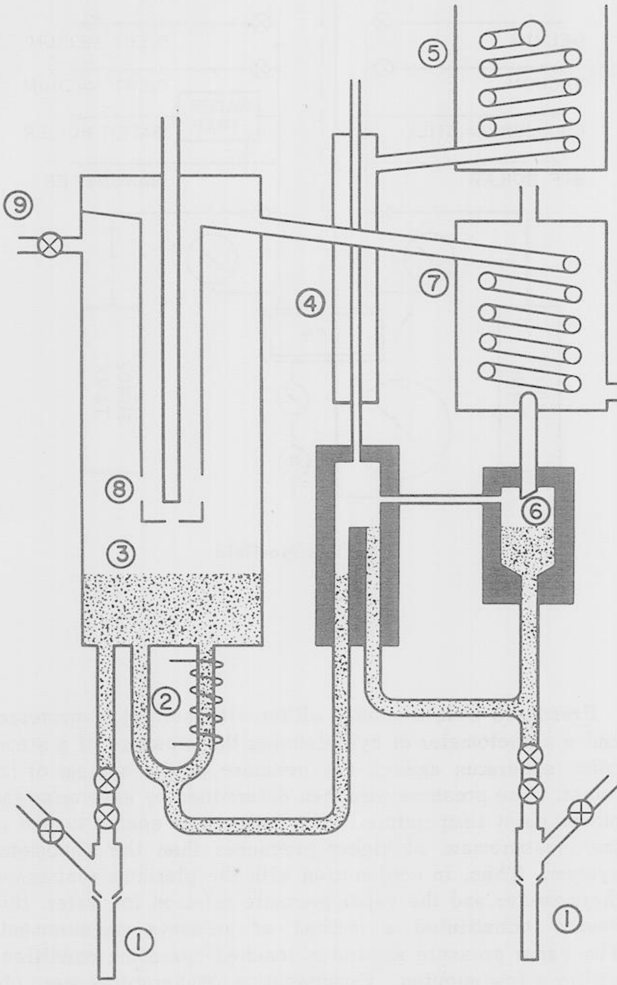

Figure 1. Equilibrium still

1. Sampling system
2. Thermosiphon heating loop
3. Boiling chamber
4. Vent condenser
5. Dry ice cooler
6. Condensed vapor sample accumulator
7. Vapor condenser
8. Jacketed thermowell
9. Loading port

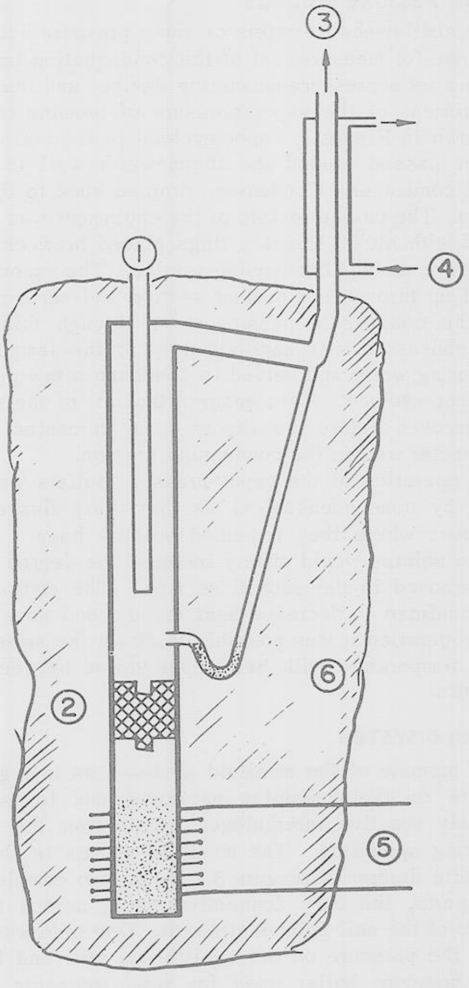

Figure 2. Vapor pressure boiler

1. Thermometer well
2. Packed section
3. To manifold
4. Cooling water inlet
5. Heater
6. Insulation

The vapors generated in the boiling chamber passed up an annulus around the thermocouple well and then to the total condenser. The vapor entered holes on the sides of the annulus rather than at the bottom to minimize entrainment. It was felt that the entrained particles could not negotiate the turn and would fall back. A small hole in the bottom closure of the annulus allowed drainage.

From the annulus surrounding the thermometer well, the vapors passed to a total condenser consisting of several turns of $^3/_8$-inch nickel tubing surrounded by a cooling water jacket. The cooling water gave a steady temperature which was cool enough to condense the halogen fluoride vapors properly, yet not freeze out the bromine trifluoride (freezing point, 8.8°C.). About 20 ml. of vapor condensate were held up in the vapor condensate receiver. This condensate holdup was held constant by a weir-type condensate level device and served as a source for vapor sampling. Vapor condensate flowed over the weir and returned to the heating loop of the boiling chamber.

The still pressure was adjusted through a vent over the condensate level device. To prevent loss of bromine pentafluoride through the vent, it was maintained at approximately -50°C. by placing a condenser around the vent. The annulus surrounding the vent tube was partially filled with Freon-12. Sufficient helium pressure existed over the Freon-12 so that it boiled at -50°C. The vapor evolved was condensed in another condenser, which was kept cold by dry ice.

Samples were drawn from the condensate receiver and boiling chamber into evacuated fluorothene tubes. The pressure over the sample was adjusted to slightly over atmospheric with helium before the fluorothene tube was disconnected and plugged. This prevented inrush of moist air from the room.

Several runs were made in the still on the system ethyl alcohol–water. The experimentally determined values were compared with the published values of Chu (*5*) taken originally from Carey and Lewis (*3*), Noyes and Warfle (*9*), and Jones and others (*7*). The average deviation of 10 samples was 0.4 %. Several runs were also made on the system toluene–*n*-heptane. The best data available on the system are those of Hipkin and Myers (*6*) and comparison was made with their data. The average deviation was 0.8 %. This agreement was at least as good as was found between the data of Hipkin and Myers (*6*) and the data of Steinhauser and White (*15*) and Bromiley and Quiggle (*2*) for this system.

VAPOR PRESSURE BOILERS

Two similar ebulliometers or vapor pressure boilers were used: one for measurement of the condensation temperature of steam as a pressure-measuring device, and the other for measurement of the vapor pressure of bromine trifluoride. As shown in Figure 2, vapor evolved in the bottom boiling section passed around the thermometer well to a water-cooled condenser. Condensate drained back to the boiling section. The unique feature of the equipment was a section packed with nickel Raschig rings placed between the boiling section and the condensing section. The vapors evolved passed up through the packed section and came in contact with the condensate passing down through this section. The condensate was approximately at the temperature of the cooling water and served to condense a few per cent of the vapor evolved. This ensured that all of the superheat was removed before the vapors came in contact with the thermometer well in the condensing section.

The operation of the vapor pressure boilers was not affected by noncondensables, as they were flushed to the condenser where they remained without harm. Any nonvolatile solutes would simply increase the degree of superheat removed in the packed section. The equipment was well insulated to decrease heat losses, and as a check of proper operation it was possible to attain the same condensation temperature with heat input varied between 30 and 300 watts.

MANIFOLD SYSTEM

The purpose of the manifold system was to regulate the pressure on the measuring apparatus and to isolate the extremely reactive interhalogen vapors from the pressure-measuring apparatus. The manifold system is shown in a schematic diagram in Figure 3. It has two completely isolated parts, the only connection being across the brass bellows of the null point instrument. One side was used to adjust the pressure on the equilibrium still and the metal vapor pressure boiler used for vapor pressure measurements on bromine trifluoride. This side of the system was filled with helium, but also contained a little interhalogen vapor that had diffused out of the interhalogen containing equipment. The other side of the manifold system controlled the pressure on the metal steam boiler used for pressure measurement, and the manometer system.

The null point instrument used to balance the pressure on the two sides of the manifold system was a Taylor differential blind manometer. This instrument is a pneumatically operated device which magnifies a difference in pressure across a brass bellows. It is supplied with approximately 20 pounds per sq. inch gage of instrument air. Its output is read on a 0- to 1500-mm. Bourdon tube gage. The instrument is adjusted so that a difference in pressure of -1 to $+1$ mm. causes the output gage to read from 1000 to 1200 mm. By adjusting the pressure on the two sides of the system until the output gage reads 1100 mm., the pressure can be equilibrated between the interhalogen and inert sides of the system to within a few hundredths of 1 mm. The amplification factor can be increased to over 100, if necessary.

MEASUREMENT OF TEMPERATURE AND PRESSURE

Temperatures were measured with a platinum resistance thermometer and a Leeds & Northrup G-2 Mueller bridge. A certificate of calibration was available for the resistance thermometer. It is doubtful whether a liquid-recirculating type of equilibrium still can give data with temperatures better than 0.1° or 0.2°C. However, it is desirable to have the vapor pressures of the pure components as accurate as possible, and in this casé an accurate instrument for temperature measurement is indispensable. In the present investigation, the measurement of pressures with a vapor pressure boiler necessitated accurate measurement of temperature.

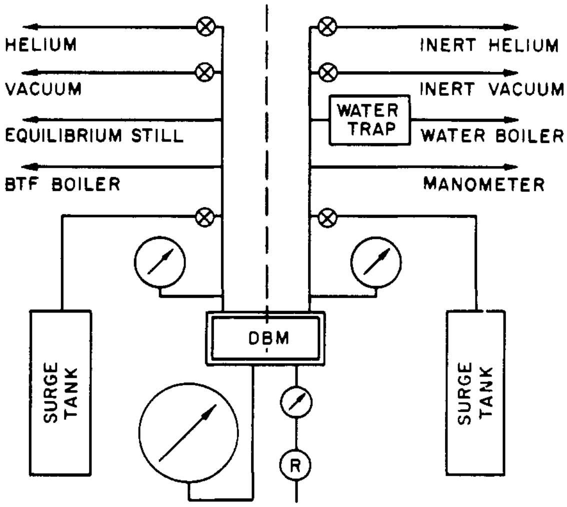

Figure 3. Manifold

Pressures were measured either with mercury manometers and a cathetometer or by balancing the pressure of a steam point apparatus against the pressure of the system of interest. The pressure was then determined by measuring the steam point temperature. The latter was easier to use in the measurement of higher pressures than the manometer system. Thus, in conjunction with the platinum resistance thermometer and the vapor pressure relation for water, this device constituted a method of pressure measurement. The vapor pressure apparatus reached operating conditions within a few minutes. Condensation temperatures were obtained with a precision of a few thousandths of a degree. Even with wide variations in boiling rate, the condensate temperature remained constant. Four data points reported on the vapor pressure of bromine pentafluoride were measured with the manometer system as a check on the operation of the vapor pressure boiler. The agreement between the two methods was excellent.

MATERIALS AND METHOD OF ANALYSIS

The interhalogens used in this investigation were purchased from the Harshaw Chemical Co. The materials were purified by distillation in an all-welded nickel still. The still pot and column head were joined to the column by means of Teflon gasketed flanges. The column diameter was approximately $\frac{5}{8}$ inch in inside diameter and packed with $\frac{1}{16}$-inch nickel helices. The column was about 2 feet long and estimated to be equivalent to 20 to 30 theoretical plates. The pressure in the purification still was controlled with a blanket of helium above the condensing vapor in the total condenser and the reflux ratio was controlled by adjusting the product take-off rate.

The purified materials were stored in prefluorinated nickel vessels under an atmosphere of helium. The pure materials were dispensed into prefluorinated vessels without contact with atmospheric moisture or with unfluorinated metal surfaces. The materials could be metered by visual observation of the liquid level in a molded fluorothene sight tube.

In establishing the purities of bromine trifluoride and and pentafluorides and in analyzing the mixtures, the refractive index measurements of Stein, Vogel, and Ludewig were used (*14*). The extreme corrosiveness of the solutions made necessary the use of a specially designed refractometer. The reported values are $n_D^{25} = 1.3529$ and

1.4536 for the pentafluoride and trifluoride, respectively. It was possible to check these values to ±0.0002, approximately the accuracy of the analytical method. The relationship between the composition of the system and the refractive in index is $n_D^{25} = 1.4536 - 0.1243x_1 + 0.0124x_1^2 + 0.0112x_1^3$, where x_1 is the mole fraction of bromine pentafluoride.

DATA AND METHOD OF CALCULATION

The Antoine equation in its original and modified form was chosen to represent the vapor pressure data of bromine pentafluoride and bromine trifluoride, respectively. These equations fit experimental vapor pressure data as well as any other empirical relationship, and are superior to other equations for extrapolation beyond the range of the experimental data. It was necessary, for use with the vapor-liquid equilibria correlation, to extrapolate the vapor pressure curve for bromine pentafluoride a few degrees above the range of the data. The vapor pressure curve for bromine trifluoride was extrapolated approximately 40° below the range of the data.

The Antoine equations are not linear in the independent variable and cannot be made so by manipulation. This makes the method of least squares a very tedious method of curve fitting to use. A method of differences very similar to that given by Weissberger (*16*) was used. One constant at a time was determined and only significant figures need be retained. The experimental vapor pressure data, including deviations from the vapor pressure equations, are given in Tables I and II for bromine pentafluoride and bromine trifluoride, respectively.

The experimental vapor pressure data on bromine pentafluoride are listed in Table I and are fitted with a modified Antoine equation. These data cannot be compared directly with the data of Ruff and Menzel (*13*) because the ranges of temperature and pressure do not overlap. However, if the modified Antoine equation is extrapolated to lower temperatures and pressures, vapor pressures are predicted that are approximately 1 % lower than those found by Ruff and Menzel. Normal boiling points are not compared, as it is probably not safe to extrapolate the data of Ruff and Menzel the required 15° or 20°C. Rogers and Speirs (*11*) report a normal boiling point of 40.76° compared to a value of 41.30°C. calculated from the data listed in Table I. It is possible that the presence of noncondensables such as hydrogen fluoride gave these investigators vapor pressures that are too high.

The experimental vapor pressure data for bromine trifluoride are listed in Table II and fitted with an Antoine equation. These data are in excellent agreement with the data presented by Oliver and Grisard (*10*). In the range above 55°C., the agreement is within 0.1 to 0.2 % in vapor pressure. They report 125.75° for the normal boiling point as compared with a value of 125.71°C. calculated from the data listed in Table II. The data given by Ruff and Braida (*12*) are in very poor agreement with the values presented here. Their vapor pressures are as much as 25 % too high. The highest pressure reported is about 140 mm. of mercury, so that normal boiling points cannot be compared. The presence of volatile impurities, such as bromine, bromine pentafluoride, and hydrogen fluoride, would cause measurements of vapor pressure to be too high with the static method that was employed.

The liquid-vapor equilibria data obtained in the Othmer still consisted of isothermal diagrams at the approximate temperatures of 50°, 75°, 100°, 125°, and 150°C. and an isobaric diagram at 1 atm. pressure. The original experimental liquid-vapor equilibria data are listed in Table III.

The liquid-vapor correlation was made for the purpose of smoothing the liquid-vapor equilibria data and calculating isotherms and isobars at even temperatures and pressures. It was assumed that the vapor phase behaves in ideal fashion. Although this assumption is not completely justified, the resulting correlation is used to calculate nearly the same information as given by the experimental data, and most of the error should cancel out. Very little would be gained in the accuracy of the calculated isotherms and isobars by estimating the nonideal behavior of the vapor phase and would add greatly to the amount of labor involved.

Table I. Vapor Pressure of Bromine Pentafluoride

Data fitted to the equation

$$\log_{10} p = 6.4545 + 0.001101t - 895/(t + 206)$$

Data collected from seven different fillings of the equilibrium still

Temp., °C.	Obsd. Pressure, Mm.	$100 \frac{(\text{Obsd. } p - \text{Calcd. } p)}{\text{Calcd. } p}$
25.073	406.21	−0.03
26.164	425.04	0.04
27.755	453.19	0.00
29.149	479.32	0.03
29.808	491.75	−0.03
30.885	513.54	0.06
33.188	561.43	0.02
34.513	590.39	−0.03
34.518	590.09	0.10
36.011	625.12	0.00
37.706	666.20	0.01
39.062	700.53	0.01
42.505	794.06	0.02
44.289	845.98	−0.01
44.391	848.67	−0.05
45.961	897.34	0.00
49.689	1020.4	−0.02
54.676	1205.8[a]	−0.01
56.643	1285.9	0.00
62.271	1537.5[a]	−0.02
64.134	1628.7	−0.02
68.222	1844.9	0.03
76.517	2348.2	−0.01
77.520	2416.5[a]	0.02
80.346	2618.4	0.15
84.995	2968.2	0.02
89.020	3303.6[a]	0.04
89.408	3334.6	−0.04
93.974	3759.0	0.16
99.658	4318.1	−0.19
104.910	4915.6	0.05
110.836	5655.6	0.17
117.842	6620.0	0.07
126.262	7939.7	−0.01
137.486	9991.7	−0.14
145.991	11,815.0	−0.03

[a] Pressure measured with mercury-in-glass manometer system.

Activity coefficients have been used in correlating liquid-vapor equilibria data. They were defined as the activity of the component in the solution divided by the mole fraction of the component. The pure component at the same temperature as the solution was taken as the standard state; thus, the activity coefficient was unity for ideal solutions. The activity coefficient may thus be regarded as a deviation factor, by considering it as the actual partial pressure of the component in the vapor divided by what the partial pressure would be if the solution were ideal.

The activity coefficients for the liquid phase of a binary mixture are related according to the well-known Gibbs-Duhem equation,

$$x_1 (d \log \gamma_1 / dx_1)_{t,P} + x_2 (d\log \gamma_2 / dx_1)_{t,P} = 0$$

This equation applies strictly only to data taken at constant temperature and pressure; however, the effect of pressure is usually negligible for pressures much less than the critical, so that the relation may be applied to data taken at constant temperature. There are several ways of using the Gibbs-Duhem equation. Plots of $\log \gamma_1$ and $\log \gamma_2$

Table II. Vapor Pressure of Bromine Trifluoride

Data fitted to the equation

$$\log_{10}p = 7.65757 - 1627.5/(t + 215)$$

Data collected from four different fillings of the ebulliometer

Temp., °C.	Obsd. Pressure, Mm.	$100\dfrac{(\text{Obsd. } p - \text{Calcd. } p)}{\text{Calcd. } p}$
63.475	65.010	−0.06
64.342	67.831	0.01
64.809	69.472	0.16
74.252	107.15	−0.23
75.049	111.26	−0.03
84.875	169.70	−0.14
85.020	171.33	0.21
94.428	250.28	0.13
94.693	252.28	−0.11
104.410	365.34	0.11
104.663	368.26	−0.03
104.690	368.78	0.02
114.026	514.57	0.07
114.264	518.96	0.09
114.354	520.14	0.01
124.965	741.74	−0.01
125.013	743.15	0.02
134.141	991.31	0.02
134.421	999.86	0.02
144.732	1359.9	0.03
144.916	1364.5	−0.16
154.429	1787.4	0.02
155.589	1844.7	0.01
164.580	2343.1	−0.03
165.223	2384.5	0.03
173.699	2954.9	0.00
180.730	3508.9	0.06
201.4[a]	5839	4.1
215.0[a]	7786	4.4
225.4[a]	9660	5.4

[a] Data not fitted to Antoine equation.

vs. x_1 may be made and the slopes, dlog γ_1/dx_1 and dlog $\gamma_2 dx_1$, compared to see how well they fit the required relation. Integration techniques may be employed to test the data in the Gibbs-Duhem equation. In the property relation which leads to the Gibbs-Duhem equation the integral of log $(\gamma_1/\gamma_2)\,dx_1$ must be zero over the whole range of composition. In a different technique one may obtain a particular solution to the Gibbs-Duhem equation and then check to see how well the data satisfy this solution. One of the more useful of the possible solutions is that of van Laar (*8*) in the form as rearranged by Carlson and Colburn (*4*). These equations are

$$\log_{10} \gamma_1 = A/(1 + Ax_1/Bx_2)^2$$

$$\log_{10} \gamma_2 = B/(1 + Bx_2/Ax_1)^2$$

In this symmetrical form, constants A and B have the property of being equal to the terminal values of log γ where the component is at infinite dilution. A and B are taken to be constants at any one temperature at which the equation is to be applied. However, A and B may be taken as functions of temperature and the resulting van Laar equations still fit the Gibbs-Duhem relation.

In the method of correlation used, values of A and B were found for each of the five isotherms. Each constant was then fitted as a function of temperature. The pair of van Laar equations together with the constants fitted as functions of temperature constituted a suitable correlation of the liquid-vapor equilibria data. This correlation was then used with the vapor pressure equations of the pure components, to predict the 1,atmosphere isobaric diagram.

The system bromine pentafluoride–bromine trifluoride offered some particular difficulties in determining the values of A and B due to the high relative volatility. The relative volatility varies from 10 to 30 over the range of conditions for which data were available. The relatively nonvolatile bromine trifluoride contributes so little to the total pressure over the solution that the pressure in turn does not offer much information concerning the activity coefficients of the trifluoride. The result is that the scatter of logarithm of the activity coefficients of bromine trifluoride is so great as to render them useless for correlation purposes.

If a method developed by Carlson and Colburn (*4*) were used, however, the high relative volatility could be used to advantage. By this method isothermal measurements of total pressure vs. liquid composition were used with the van Laar equations to calculate equilibrium liquid and vapor compositions. From the definition of the activity coefficients, it followed that

$$\gamma_1 = (P - \gamma_2 p_2 x_2)/p_1 x_1$$

As x_2 approaches 1.0, γ_2 approaches 1.0, so that the activity coefficient of component 1 can be calculated by assuming $\gamma_2 = 1$. This is especially true in this case, since p_2, the vapor pressure of bromine trifluoride, is small and minimizes any error caused by assuming $\gamma_2 = 1$.

The above method worked very well for calculating A, but did not work at all with B and another method had to be found. This was done simply by trial and error. B was chosen such that when it was used with the correlation, the calculated total pressures agreed most closely with the experimentally observed data.

The constants of the van Laar equations were fitted with the equations,

$$A = 0.1290 + 0.001076t$$

$$B = 0.4000 + 0.001000t$$

The observed values of A and B are listed in Table IV. The deviations from the above equations are also listed.

Table IV. Constants of Van Laar Equations

t, °C.	Obsd. A	Obsd. A − Calcd. A	Obsd. B	Obsd. B − Calcd. B
50	0.188	0.005	0.450	0.000
75	0.222	0.012	0.450	−0.025
100	0.192	−0.045	0.500	0.000
125	0.274	0.010	0.540	0.015
150	0.313	0.023	0.550	0.000

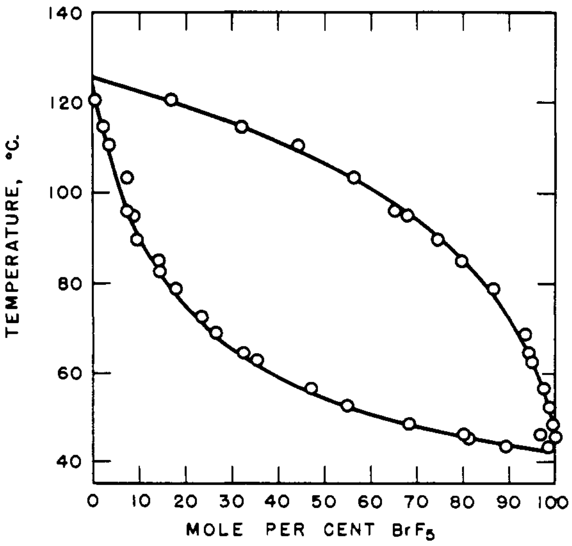

Figure 4. Liquid-vapor equilibria

1 atm., isobar system BrF_5–BrF_3
Data adjusted to 1 atm.

Table III. Vapor-Liquid Equilibrium Data for System Bromine Pentafluoride-Bromine Trifluoride

Mole % BrF_5		Temp., °C.	Pressure, Mm. Hg	Activity Coefficient, γ	
Liquid	Vapor			BrF_5	BrF_3
20.6	92.4	49.7	331	1.48	0.98
22.5	91.0	53.0	385	1.36	1.16
29.7	96.1	49.8	446	1.41	0.76
39.3	96.0	50.0	546	1.29	1.10
44.9	96.3	49.5	598	1.26	1.25
56.0	97.6	49.9	711	1.21	1.19
62.3	98.3	50.0	769	1.18	1.06
85.9	99.0	50.0	927	1.04	2.00
91.3	99.5	50.0	962	1.01	1.68
6.7	70.5	75.0	352	1.65	1.00
12.0	82.0	74.9	522	1.58	0.97
18.0	82.9	75.3	680	1.38	1.26
19.4	88.4	74.9	748	1.52	0.98
20.9	89.5	75.1	753	1.43	0.90
27.0	....	74.1	889	....	....
24.6	90.9	74.6	902	1.50	1.00
28.7	....	75.5	1022	....	....
35.9	94.9	74.9	1172	1.38	0.84
37.9	93.4	75.3	1214	1.32	1.14
41.0	95.0	74.7	1258	1.31	0.97
43.6	94.9	74.8	1352	1.32	1.11
52.0	94.4	75.0	1476	1.19	1.56
54.8	....	75.3	1556	....	....
57.4	95.2	75.2	1572	1.15	1.58
67.3	98.0	74.7	1754	1.15	1.00
69.3	98.5	75.0	1786	1.13	0.80
71.2	97.6	74.7	1811	1.11	1.39
84.9	99.0	74.9	2017	1.05	1.17
93.4	99.6	75.0	2148	1.02	1.18
0.6	24.6	100.0	414	3.95	1.01
4.8	51.8	100.0	611	1.52	1.00
9.4	67.0	100.5	855	1.37	0.99
13.1	75.9	99.8	1109	1.48	1.12
15.5	78.0	100.2	1307	1.49	1.09
16.9	81.4	99.6	1342	1.50	0.98
22.5	86.3	99.7	1592	1.41	0.92
24.5	86.8	100.2	1853	1.50	1.04
32.8	87.5	100.4	2212	1.34	1.31
35.2	91.1	100.7	2364	1.38	1.02
38.5	93.0	100.3	2491	1.37	0.91
48.1	93.1	100.0	2834	1.26	1.22
54.5	92.2	99.8	3072	1.20	1.72
63.2	96.4	99.5	3312	1.17	1.07
73.5	98.0	100.3	3667	1.11	0.88
77.4	98.9	99.8	3680	1.08	0.56
86.4	99.4	100.1	4034	1.06	0.54
93.2	99.6	100.0	4176	1.02	0.89
1.9	26.8	125.0	994	1.77	1.00
7.2	55.1	123.9	1549	1.58	1.05
9.4	63.9	125.3	1971	1.73	1.05
13.6	73.1	123.9	2418	1.72	1.05
17.7	76.7	123.6	2715	157	1.09
18.1	77.2	125.2	2997	1.64	1.19
....	87.4	123.6	3943	....	....
34.2	90.3	123.3	4252	1.50	0.89
35.9	88.9	124.9	4495	1.44	1.06
47.2	91.0	125.0	5289	1.32	1.22
54.1	94.0	125.3	5601	1.38	0.81
50.0	94.7	124.9	5629	1.25	1.04
....	94.3	124.7	5747	....	....
58.4	94.8	124.9	5996	1.26	1.02
....	95.5	123.2	6192	....	....
73.6	96.6	125.1	6704	1.14	0.34
80.9	96.9	125.1	6971	1.08	1.50
81.6	98.6	125.0	7058	1.10	0.74
91.6	99.3	124.9	7358	1.03	0.84
92.6	99.2	125.0	7394	1.03	1.03
3.5	38.4	150.0	2564	2.18	1.04
3.6	42.6	149.9	2603	2.40	0.98
7.0	54.9	150.4	3250	1.99	0.99
13.2	68.9	150.0	4429	1.81	1.00
21.1	78.5	149.9	5904	1.73	1.02
23.2	81.0	150.0	6038	1.66	0.94
24.7	79.7	149.8	6079	1.54	1.04
33.7	....	149.8	7309	....	....
34.5	84.5	149.8	7460	1.44	1.13
45.8	85.2	150.7	9084	1.90	0.94
52.3	91.0	149.8	9500	1.30	1.14
59.0	94.5	150.2	10228	1.28	0.86
76.4	96.9	149.6	11312	1.14	1.06
97.0	100.0	150.0	12522	1.01	....
89.8	98.7	43.6	763	1.02	4.30
81.1	100.0	45.6	761	1.06	....
80.6	96.8	45.9	761	1.02	4.74
68.6	99.7	48.2	760	1.14	0.23
54.8	98.4	52.6	759	1.06	0.72
47.1	97.5	56.2	761	1.24	0.79
34.6	94.9	62.8	736	1.29	0.92
32.2	94.1	64.4	760	1.35	0.97
26.4	93.2	69.0	760	1.42	0.83
22.9	....	72.7	743	....	....
17.7	86.5	78.9	760	1.48	0.95
14.4	....	82.4	759	1.41	1.07
14.4	79.4	85.1	760	....	....
9.5	74.2	89.8	758	1.75	1.04
8.7	67.9	95.1	760	1.53	1.04
7.9	65.0	96.1	758	1.58	5.98
7.4	56.5	103.5	760	1.21	1.02
3.3	42.6	110.4	741	1.69	0.89
2.0	30.2	114.4	742	1.88	1.02
0.4	15.6	120.5	749	4.05	0.99

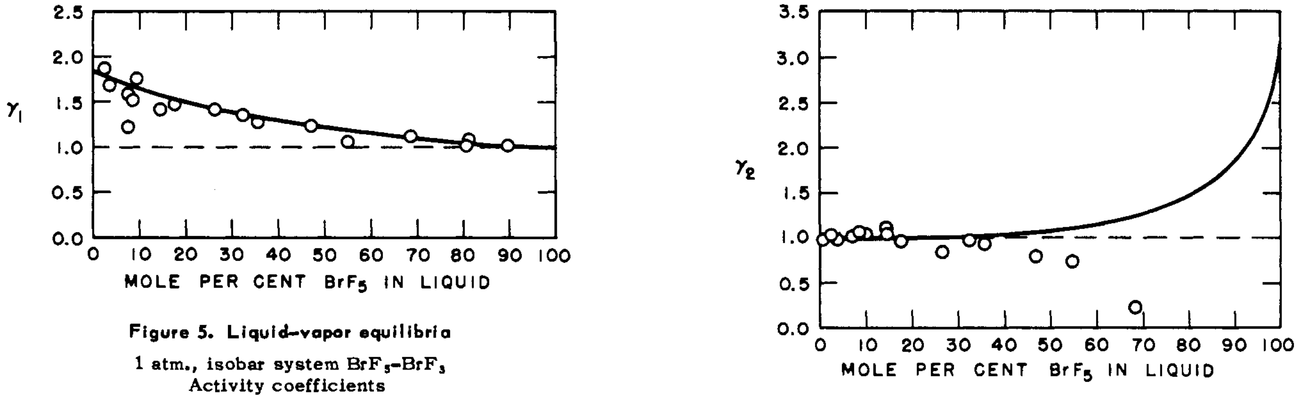

Figure 5. Liquid-vapor equilibria

1 atm., isobar system BrF_5-BrF_3
Activity coefficients

The calculated 1-atm. diagram is compared with the experimentally observed data at 1 atm. in Figure 4. The activity coefficients calculated from the correlation are compared with the observed values in Figure 5. The coefficients for the more volatile bromine pentafluoride are in good agreement with the van Laar equations, while those for the trifluoride deviate somewhat at high pentafluoride concentrations. This is to be expected, however, because small errors in measuring the concentration of the less volatile trifluoride are magnified many times in the activity coefficients. Thus, if the van Laar equations are used to calculate the vapor and liquid concentrations, the results will agree very closely with the experiments.

NOMENCLATURE

x_1, x_2 = mole fraction of bromine pentafluoride and bromine trifluoride in liquid phase, respectively
y_1, y_2 = mole fraction of bromine pentafluoride and bromine trifluoride in vapor phase, respectively
P_1, P_2 = vapor pressure of pure bromine pentafluoride and bromine trifluoride, respectively, at temperature of solution
P = total pressure over solution
t = temperature, °C.
$\gamma_1 = Py_1/p_1x_1$, activity coefficient of bromine pentafluoride
$\gamma_2 = Py_2/p_2x_2$, activity coefficient of bromine trifluoride
A = limit ($\log_{10} \gamma_1$) as x_1 approaches zero, a constant of van Laar equations
B = limit ($\log_{10} \gamma_2$) as x_2 approaches zero, a constant of van Laar equations

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Heat Capacity of Saturated Liquid Perchloryl Fluoride above Its Boiling Point

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A program at the Pennsalt Chemicals Corp. has been concerned with determination of physical properties of perchloryl fluoride (ClO_3F) (*3,8*). The present report deals with the saturated heat capacity of the liquid from the boiling point to the critical region. No previous measurements of the heat capacity of perchloryl fluoride have been reported in the literature.

APPARATUS

Calorimeter and Cryostat. The calorimeter (Figure 1) was designed to be used at vapor pressures up to 60 atm. The calorimeter, *A*, was fabricated from a 4-inch length of 1-inch nickel pipe with all joints silver-soldered and had an internal volume of 58.79 cc. Radiation shield *B* was an 8-inch length of 2½-inch copper pipe, with ⅛-inch plate ends. The outer container, *C*, was made from 4½-inch brass tubing of ⅛-inch wall with ⅛-inch end plates.

A 20-ohm length of B. & S. gage No. 36 double silk-covered Constantan wire, which served as a heater, was wound on the outer surface of the calorimeter. Also wrapped on the calorimeter was a 10-ohm length of B. & S. gage No. 40 double Formvar-coated copper wire to serve as a thermometer. Paired voltage and current leads of No. 36 B. & S. gage double silk-covered copper wire were attached to the heater and copper thermometer. The radiation shield was wound with approximately 100 ohms of No. 36 B. & S. gage Constantan wire, which served as a heater.

All leads and thermocouple wires, as well as the wires wrapped on the calorimeter and shield, were impregnated with Formvar lacquer and baked. The outer surface of the calorimeter, both surfaces of the radiation shield, and the inner surface of the outer container were covered with aluminum foil.

A tube connection, *F*, through the top plate of the outer container allowed passage of the wire leads. The seal at this point was made by a device developed by Johnston and Kerr (*4*). A standard 24/40 female ground-glass joint was fitted with a Lucite plug, in whose surface vertical grooves had been machined. The lead wires were laid in these grooves and carefully sealed in position with Apiezon W wax, so that the plug formed a vacuum-tight seal with the ground-glass joint. This was an easily prepared and excellent vacuum seal. A second tube connection, *H*, provided access to a vacuum system capable of 10^{-5} mm. of mercury or better and to a helium source.

The entire assembly was placed in a constant temperature bath which could be controlled to ±0.10° above 25° and to ±0.50° to −40°C.

Electrical Circuits. The general plan of electrical circuits for energy supply and for the resistance and thermocouple measurements was similar to that described by Gibson and Giauque (*2*), except that the thermometer and heater were separate units.