Dew and Bubble Points of Simulated Natural Gases

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Experimental dew and bubble points and densities of the saturated phase envelopes for 10 simulated natural gas samples are presented. The effect of helium on the phase behavior of natural gases is also illustrated.

THIS study was undertaken to obtain data on the physical properties of natural gases at cryogenic conditions. The gases tested are multicomponent mixtures representing one lean and one rich natural gas. To provide a means of isolating the effect of the various components on the physical properties of natural gas, each natural gas was investigated as a series of compositions. A mixture of nitrogen, methane, ethane, and propane was prepared initially in the same ratio as in the natural gas, from which a complete set of test results was obtained. Butane was then added, and its effect on the properties of natural gas was studied. The pentanes were then added and so on, up to heptane. In this way, the properties of the mixtures were studied.

APPARATUS

The apparatus used for this work is a modified version of a phase equilibria cell described before (*1, 2*). A schematic flow diagram is presented in Figure 1. The equilibrium cell is presented in Figure 2.

As shown in Figure 1, sample fluid is stored in a 3-liter reservoir (*B*) and compressed by two 250-cc. Jerguson gages (*C, D*). Mercury lines run from the bottom of the gages to a high-pressure mercury injection pump (*G*) and a 3-liter mercury reservior (*E*). To avoid stratification, multicomponent samples are mixed by a recirculation pump (*F*) (*3*).

The pressure measurements are obtained from a 2000-p.s.i. Heise gage (*H*) to within ±2 p.s.i. and from a 5000-p.s.i. dead-weight tester (*K*) to within ±0.1 p.s.i. The Heise gage was used to obtain approximate values of the experimental pressure, and the dead-weight tester was used to determine the exact value of this pressure. The measurements were made through the mercury separator (*J*) with a sensitivity exceeding the ±0.1 p.s.i. sensitivity of the dead-weight tester. A correction was made for the hydrostatic head of the oil in the 2-foot line from the separator to the dead-weight tester.

Thermostatic conditions for the observations are achieved by placing the phase cell (*L*) inside a 2.5-gallon Dewar flask containing a fluid—usually isopentane or propane—kept at a constant temperature. Temperature is controlled by a copper coil, through which a regulated amount of liquid nitrogen flows, and by a heating element regulated by a Bailey temperature controller. The thermostatic fluid is stirred with a squirrel-cage fan driven by an electric motor. The arrangement permits control of the temperature to within ±0.05° F. of the set point.

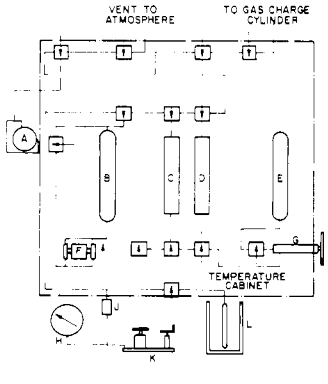
The temperature of the bath, assumed to be the same as that of the sample in the glass cell at equilibrium, is measured by a calibrated copper-constantan thermocouple. The thermocouple was calibrated against a platinum resistance thermometer at 50° F. intervals over the range of +100° to −320° F. The platinum resistance thermometer used is a Rosemount engineering temperature standard with calibration traceable to NBS. The e.m.f. produced by the thermocouple is balanced with a Leeds and Northrup K-2 potentiometer with a reference cold junction kept at 32° F. The state of balance is shown by a Leeds and Northrup Type E deflection galvanometer. Temperatures can be accurately read to within ±0.04° F.

Dew and bubble points are determined visually in a borosilicate glass cell. The fluid inside the cell is agitated by raising and lowering an enclosed steel ball with a U magnet.

Densities of the dew and bubble point fluids are calculated from the calibrated volume of the glass cell and the amount

Figure 1. Schematic of dew and bubble point apparatus

- A. Vacuum pump
- B. Sample fluid reservoir
- C. Jerguson gage
- D. Jerguson gage
- E. Mercury reservoir
- F. Magnetic pump
- G. Mercury injection pump
- H. Heise gage
- I. Separator
- J. Dead-weight tester
- K. Phase cell and thermostat



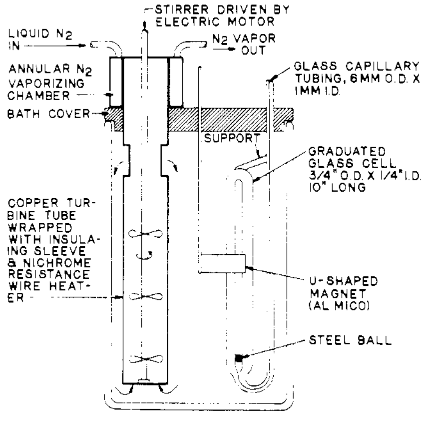


Figure 2. Equilibrium cell, low-temperature bath assembly

Table I. Quality of Material Used

Components	Purity, Mole	Source	Grade
Nitrogen	99.99	Matheson	Prepurified
Methane	99.95	Matheson	Ultra-Pure
Ethane	99.97	Phillips 66	Research
Propane	99.90	Phillips 66	Research
n-Butane	99.91	Phillips 66	Research
n-Pentane	99.98	Phillips 66	Research
Hexane	99.0	Phillips 66	Pure
Heptane	99.0	Phillips 66	Pure

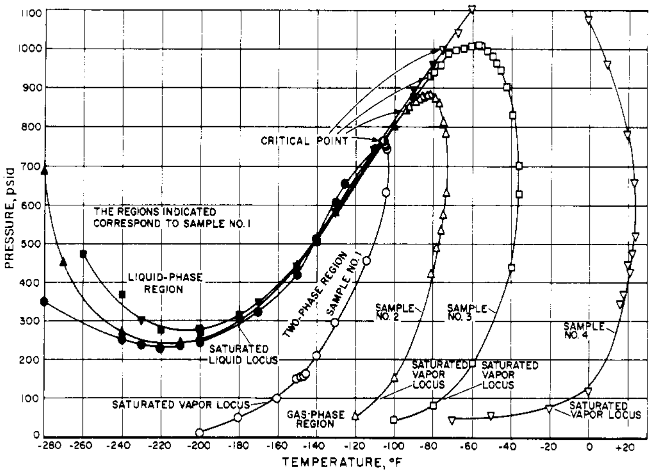


Figure 3. Dew and bubble points for natural gas samples Nos. 1, 2, 3, and 4

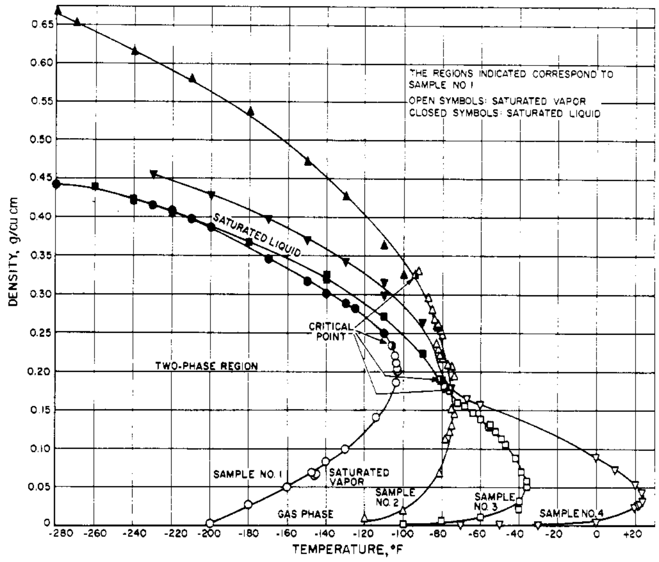


Figure 4. Saturated vapor-liquid densities for natural gas samples Nos. 1, 2, 3, and 4

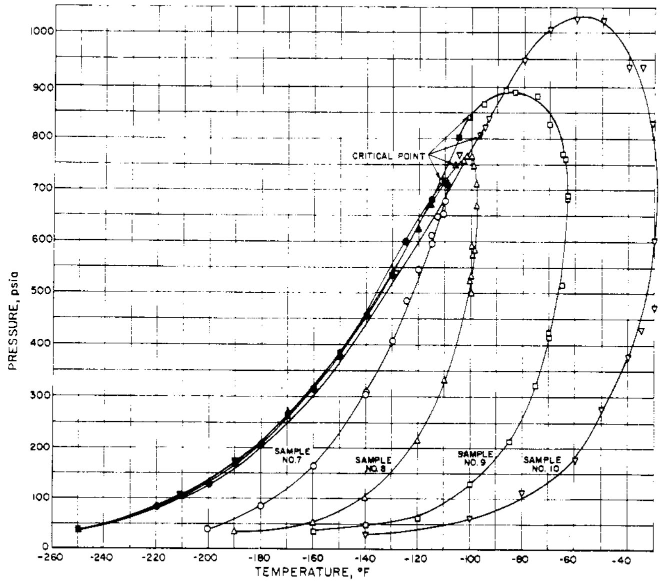


Figure 5. Dew and bubble points for natural gas samples Nos. 7, 8, 9, and 10

of gas displaced at the temperature and pressure of the Jerguson gage. The quality of the material used is presented in Table I.

EXPERIMENTAL

The mass spectrographic analysis of the gases studied in the dew and bubble point apparatus is shown in Table II. Figure 3 shows comparison of the envelopes of the

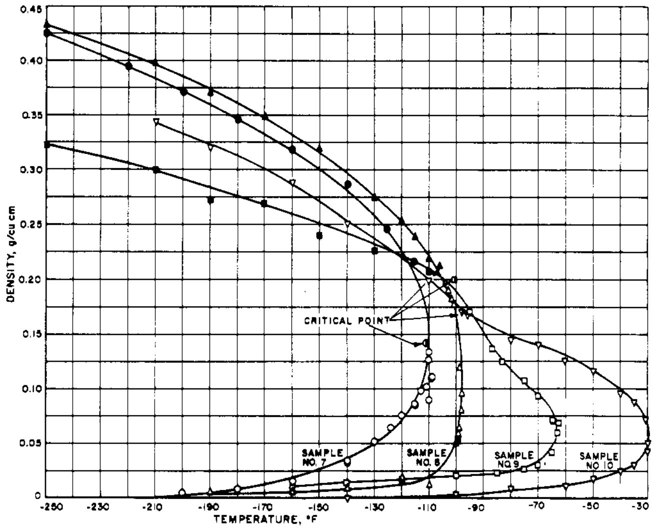


Figure 6. Saturated vapor-liquid densities for natural gas samples Nos. 7, 8, 9, and 10

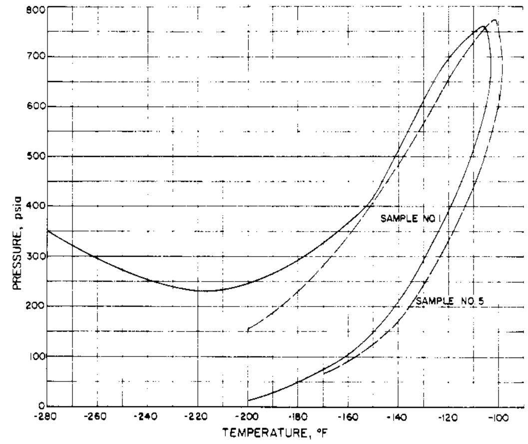


Figure 7. Two-phase envelopes for samples Nos. 1 and 5

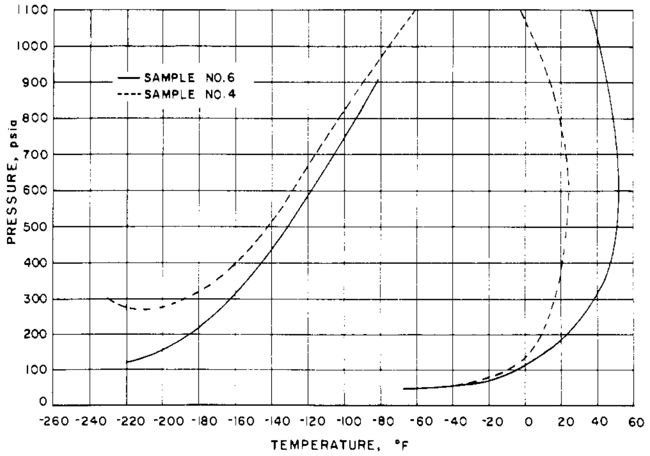


Figure 8. Dew and bubble points for natural gas samples Nos. 4 and 6

Table II. Analyses of Gas Samples

	Sample No.; Mole %									
Constituent	1	2	3	4	5	6	7	8	9	10
N_2	3.80	3.30	3.40	3.40	3.30	3.10	1.50	1.60	1.60	1.40
He	0.07	0.14	0.18	0.17	...	...	...	...	...	...
CH_4	91.70	88.70	86.80	86.20	91.00	81.40	95.90	95.00	94.50	94.30
C_2H_6	4.30	6.60	6.50	6.40	5.60	11.10	2.60	2.60	2.60	2.70
C_3H_8	0.04	1.30	2.50	2.40	0.12	1.80	0.01	0.78	0.81	0.74
C_4H_{10}	...	...	0.65	0.46	...	0.26	...	...	0.52	0.49
C_5H_{12}	...	...	...	0.09	...	...	...	...	...	0.10
C_6H_{14}	...	...	...	0.87	...	2.30	...	...	...	0.27
C_7H_{16}	...	...	...	0.01	...	...	...	...	...	...
Total	99.91	100.04	100.03	100.00	100.02	99.96	100.01	99.98	100.03	100.00

Table III. Experimental Dew and Bubble Points for Natural Gas Samples

Dew Points			Bubble Points		
Press., p.s.i.a.	Temp., ° F.	Density, g./cc.	Press., p.s.i.a.	Temp., ° F.	Density, g./cc.
SAMPLE 1					
14.0	−200.0	0.004	738.0	−110.0	0.249
55.1	−180.0	0.026	656.5	−125.0	0.282
98.1	−160.0	0.050	608.8	−130.0	0.289
151.3	−150.0	0.068	512.5	−140.0	0.301
158.8	−147.5	0.068	445.0	−150.0	0.316
159.8	−146.0	0.063	337.5	−170.0	0.345
165.0	−145.0	0.067	245.0	−200.0	0.387
211.6	−140.0	0.083	236.5	−210.0	0.397
299.6	−130.0	0.098	231.0	−220.0	0.408
455.5	−114.0	0.142	240.2	−230.0	0.414
635.5	−104.3	0.186	251.2	−240.0	0.424
738.0	−103.2	0.200	348.0	−280.0	0.442
747.0	−103.8	0.206			
751.2	−103.9	0.210			
769.7	−104.7	0.222			
763.8[a]	−106.0	0.234			
SAMPLE 2					
54.2	−120.0	0.008	801.9	−100.0	0.324
150.0	−100.0	0.018	732.9	−110.0	0.366
342.3	−80.0	0.050	733.9	−110.0	0.362
421.4	−81.2	0.067	582.1	−130.0	0.426
487.7	−78.3	0.111	442.9	−150.0	0.471
534.7	−76.0	0.121	303.1	−180.0	0.522
571.7	−75.0	0.129	303.1	−180.0	0.537
630.4	−73.5	0.145	241.4	−210.0	0.579
782.2	−73.4	0.194	270.9	−240.0	0.614
804.7	−75.0	0.206	450.9	−270.0	0.652
810.7	−75.0	0.177	689.9	−280.0	0.666
859.2	−77.0	0.208			
892.2	−80.0	0.246			
884.2	−81.0	0.253			
878.4	−81.7	0.255			
877.6	−81.9	0.260			
877.2	−81.9	0.140			
873.2	−83.0	0.205			
871.7	−85.0	0.223			
873.2	−85.6	0.226			
867.2	−80.0	0.216			
868.4	−81.0	0.220			
864.4	−82.0	0.228			
871.7	−83.0	0.236			
879.7	−83.0	0.260			
875.7	−84.0	0.267			
872.2	−85.0	0.278			
869.7	−87.0	0.294			
860.2	−89.0	0.307			
849.7	−92.0	0.328			
840.7[a]	−93.9	0.325			
SAMPLE 3					
45.4	−100.0	0.002	875.9	−90.0	0.223
82.6	−80.0	0.005	726.4	−110.0	0.272
190.1	−60.0	0.010	507.3	−140.0	0.325
436.9	−40.0	0.022	510.3	−140.0	0.318
439.9	−40.0	0.033	315.4	−180.0	0.366
628.6	−36.0	0.051	269.6	−200.0	0.386
703.3	−36.1	0.058	282.4	−200.0	0.383
830.6	−38.8	0.070	276.4	−220.0	0.404
903.4	−42.0	0.088	368.9	−240.0	0.421
962.9	−47.0	0.106	473.8	−260.0	0.439
980.9	−49.0	0.114			
994.9	−52.0	0.122			
1006.1	−55.0	0.132			
1005.4	−55.0	0.124			
1008.0	−56.0	0.129			
1008.4	−56.0	0.128			
1007.4	−60.0	0.138			
1000.9	−64.0	0.147			
995.6	−68.0	0.155			
988.4	−72.0	0.159			
957.4	−76.0	0.175			
938.4	−78.9	0.182			
934.6	−81.1	0.187			
930.9[a]	−81.3	0.191			
SAMPLE 4					
46.4	−70.0	0.002	962.9	−80.0	0.191
57.4	−50.0	0.003	895.9	−90.0	0.265
74.6	−20.0	0.002	747.9	−110.0	0.315
122.6	0.0	0.006	747.4	−110.0	0.298
346.9	+16.1	0.016	589.9	−130.0	0.343
373.1	+18.0	0.018	444.6	−150.0	0.371
447.9	+20.0	0.025	350.9	−170.0	0.397
429.6	+21.4	0.028	279.3	−200.0	0.428
476.6	+22.5	0.030	302.6	−230.0	0.455
523.6	+24.0	0.033			
660.4	+23.5	0.044			
784.3	+20.0	0.054			
962.6	+10.0	0.074			
1076.4	0.0	0.090			
1104.4	−60.0	0.159			
1042.3	−67.0	0.167			
999.4[a]	−75.2	0.17			
SAMPLE 5					
67.4	−170.0	0.006	760.1	−104.4	0.209
123.6	−150.0	0.009	721.6	−110.0	0.235
215.9	−130.0	0.016	747.4	−110.0	0.235
241.6	−130.0	0.023	644.9	−120.0	0.258
434.9	−110.0	0.043	475.9	−140.0	0.302
643.9	−100.0	0.074	337.6	−160.0	0.329
804.6	−98.0	0.141	233.6	−180.0	0.348
781.9	−99.0	0.147	152.4	−200.0	0.348
776.4	−100.0	0.154			
774.6[a]	−101.0	0.161			

[a] Critical point.

(Continued)

Table III. Experimental Dew and Bubble Points for Natural Gas Samples (*Continued*)

Dew Points			Bubble Points		
Press., p.s.i.a.	Temp., ° F.	Density, g./cc.	Press., p.s.i.a.	Temp., ° F.	Density, g./cc.
		SAMPLE 6			
45.4	−70.0	0.006	913.9	−80.0	0.275
61.4	−50.0	0.007	745.1	−100.0	0.316
69.6	−20.0	0.005	582.9	−120.0	0.350
112.6	0.0	0.008	433.6	−140.0	0.375
190.4	20.0	0.010	313.4	−160.0	0.394
244.6	30.0	0.053	186.4	−190.0	0.432
277.4	35.0	0.054	121.6	−220.0	0.455
333.4	40.0	0.058			
378.4	44.0	0.061			
419.6	47.0	0.063			
521.9	51.0	0.070			
609.4	51.7	0.077			
649.9	51.0	0.081			
732.9	49.0	0.082			
816.9	45.0	0.083			
816.6	45.0	0.082			
1143.4	35.0	0.090			
		SAMPLE 7			
41.4	−200.0	0.005	683.1	−115.0	0.216
84.6	−180.0	0.009	598.6	−125.0	0.244
161.6	−160.0	0.017	457.3	−140.0	0.285
305.5	−140.0	0.033	315.5	−160.0	0.318
306.4	−140.0	0.034	210.1	−180.0	0.346
407.1	−130.0	0.052	129.6	−200.0	0.372
483.4	−124.0	0.064	81.8	−220.0	0.396
542.6	−119.8	0.075	37.4	−250.0	0.425
610.9	−115.0	0.088			
596.8	−115.5	0.085			
648.6	−113.0	0.099			
654.4	−111.0	0.104			
678.9	−110.0	0.090			
714.4	−109.0	0.109			
710.9	−109.1	0.116			
715.6	−109.6	0.126			
714.9	−110.2	0.133			
715.0^a	−110.7	0.142			
715.7^a	−110.7	0.142			
		SAMPLE 8			
35.4	−190.0	0.006	715.8	−110.0	0.219
55.4	−160.0	0.006	672.8	−115.0	0.239
101.6	−140.0	0.009	626.2	−120.0	0.253
217.0	−120.0	0.019	537.2	−130.0	0.275
331.7	−110.0	0.012	378.2	−150.0	0.318
592.6	−100.0	0.049	269.9	−170.0	0.348
590.5	−100.0	0.050	170.1	−190.0	0.370
526.7	−99.8	0.053	106.1	−210.0	0.397
526.7	−99.8	0.056	37.4	−250.0	0.433
577.6	−99.0	0.064			
582.3	−99.0	0.058			
670.9	−97.6	0.080			
714.5	−98.0	0.096			
747.1	−99.0	0.119			
764.5	−100.5	0.177			
765.5	−102.0	0.182			
757.6	−103.2	0.190			
751.4^a	−105.9	0.212			
751.2^a	−105.9	0.208			
		SAMPLE 9			
34.4	−160.0	0.011	753.8	−105.0	0.179
49.4	−140.0	0.013	713.0	−110.0	0.205
62.4	−120.0	0.017	533.7	−130.0	0.226
130.6	−100.0	0.020	375.9	−150.0	0.240
214.1	−85.0	0.023	261.1	−170.0	0.268
323.8	−75.0	0.027	169.6	−190.0	0.272
421.7	−70.0	0.032	106.4	−210.0	0.300
414.6	−70.0	0.032	37.2	−250.0	0.322
516.9	−65.0	0.043			
688.4	−63.0	0.060			
685.8	−63.0	0.069			
713.4	−64.0	0.070			
720.6	−65.0	0.071			
780.9	−70.0	0.093			
830.9	−75.0	0.107			
839.9	−83.0	0.124			
841.4	−86.8	0.137			
815.0	−95.0	0.171			
791.6^a	−100.5	0.199			
790.9^a	−100.5	0.198			
		SAMPLE 10			
30.4	−140.0	0.003	768.4	−105.0	0.171
62.4	−100.0	0.006	720.4	−110.0	0.200
114.1	−80.0	0.009	536.0	−130.0	0.252
178.8	−60.0	0.013	311.4	−160.0	0.289
277.3	−50.0	0.020			
378.9	−40.0	0.027	163.4	−190.0	0.321
604.4	−30.0	0.051	105.4	−210.0	0.343
431.2	−35.0	0.031			
473.8	−30.0	0.044			
831.7	−31.0	0.073			
940.4	−35.0	0.089			
941.2	−40.0	0.097			
1028.4	−50.0	0.118			
1029.6	−60.0	0.127			
1010.4	−70.0	0.142			
948.6	−80.0	0.146			
840.0	−93.9	0.158			
822.4	−95.7	0.169			
809.1^a	−97.7	0.171			

first four mixtures, and Figure 4 compares the saturated vapor-liquid densities for the same mixtures.

Figure 5 shows the envelopes of mixtures Nos. 7 to 10, and Figure 6 compares their saturated vapor-liquid densities.

The peculiar effect of helium on the behavior of the first four mixtures was analyzed by experimental determination on two helium-free mixtures (samples 5 and 6) with compositions similar to the first and fourth samples. Figure 7 compares the behavior of sample 5 with that of sample 1. Similar results were obtained with sample 6 (Figure 8). The displacement of the envelope of mixture 6 was caused by its high ethane content.

The helium content of the four gases previously investigated caused the increase of the bubble point pressure at temperatures below −200° F. The process which causes this increase appears to be the preferential condensation of the hydrocarbons with an increase in the percentage of helium in the gaseous phase.

Experimental data are presented in Table III. Because of the scarcity of comparable literature data, the data reported must be judged by its internal consistency and by the magnitude of the errors inherent to the equipment used. Based on these considerations, it is concluded that the dew-and-bubble point data is accurate to ±0.1° F. and ±0.3 p.s.i. The saturated vapor densities are believed to be accurate to ±1.5% while the saturated liquid densities are accurate to ±1.0%.

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Thermodynamic Functions of Thionyl Bromide

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The thermochemistry of thionyl bromide was investigated at 25° C. in a conventional reaction calorimeter. The standard enthalpy of formation of the liquid is −40.2 ± 0.3 kcal. per mole and statistical thermodynamic functions are calculated for the gas.

THE CHEMISTRY of the thionyl halides (SOX_2) has been included in a recent review (*2*). The thermal stability of these compounds decreases with increasing molecular weight, and this fact is reflected in the thermodynamic and structural data available.

Experiments on the photodecomposition of thionyl bromide by Hussain and Samuel (*5*) give two estimates (*14*) for $\Delta H_f^\circ[SOBr_2, g]$, −21.8 and −27.2 kcal. per mole. The updated version (*15*) of the National Bureau of Standards Circular 500 (*10*) reports the datum $\Delta H_f^\circ[SOBr_2, g] = -17.7$ kcal. per mole. The source of this latter figure is not clear. The value reported here diverges widely from the above. A conventional reaction calorimeter has been utilized to investigate the aqueous hydrolysis of thionyl bromide at 25° C. and molecular structure and spectroscopic data were used to calculate thermodynamic functions in the gas phase.

EXPERIMENTAL

Materials. Thionyl bromide was prepared by the method of Hibbert and Pullman (*4*) which involved passing dry hydrogen bromide gas through thionyl chloride. The product distilled at 39° C./15 mm. of Hg as an orange-yellow liquid. It was redistilled at 0.1 mm. of Hg as a clear yellow liquid and stored at −20° C. Found: Br, 76.6; Calculated for $SOBr_2$: Br, 76.9%.

Calorimeter. This was of the constant-temperature-environment type fully immersed in a thermostat maintained at 25.0 ± 0.01° C. Details of construction may be found elsewhere (*1*). Thermal leakage corrections were made by the equal areas method, which is satisfactory (*8*) when a net precision of ±0.5% is required. The precision and accuracy of the equipment were assessed by two standard reactions, one exothermic and the other endothermic. For the enthalpy of neutralization of tris(hydroxymethyl)-aminomethane (THAM) in excess 0.1*M* hydrochloric acid, the mean of seven determinations was −7.15 ± 0.03 kcal. per mole at 25° C. and $n = 600$ [lit. (*3*), −7.107 ± 0.004 kcal. per mole at 25° C. and $n = 1350$]. The enthalpy of dilution of THAM is negligible. For the enthalpy of solution of potassium chloride in water, the mean of five determinations was +4.23 ± 0.02 kcal. per mole at 25° and $n = 200$ [lit. (*3*), 4.200 ± 0.009 kcal. per mole at 25° C. and $n = 200$]. n is the mole ratio of water to solute. The precision of the electrical calibration was ±0.1%. This error was an order of magnitude smaller than the error in the observed heats of hydrolysis and, hence, was ignored. The limiting feature on the accuracy of the results reported here is the purity of the thionyl bromide at reaction time. Further details of the electrical calibration procedure are given in Reference (*1*). Enthalpies are reported in terms of the defined thermochemical calorie—1 cal. = 4.1840 abs. joule.

RESULTS

Thionyl bromide hydrolyzed rapidly and quantitatively, but without undue violence, according to the following equation:

$$SOBr_2(liq.) + (n + 1)H_2O(liq.) = [SO_2 + 2HBr]nH_2O$$

Hence,

$$\Delta H_f^\circ[SOBr_2, liq.] = 2\Delta H_f^\circ[HBr, \tfrac{n}{2}H_2O] + \Delta H_f^\circ[SO_2 nH_2O] - \Delta H_f^\circ H_2O(liq) + \Delta H_{mix} - \Delta H_{obsd}$$

where ΔH_{obsd} is the observed enthalpy of hydrolysis and ΔH_{mix} is the enthalpy of mixing of the products of hydrolysis (Table I). This latter term is small and may be estimated from the data of Johnson and Sunner (*7*). These workers measure the heat of mixing of aqueous hydrobromic acid with an aqueous sulfuric acid–sulfur dioxide solution. Selecting $n = 1240$ and ignoring the effect of the sulfuric acid, Sunner and Johnson's Equation 5 may be combined with:

$$[HBr\ 5.59H_2O] + 614.4H_2O = [HBr\ 620H_2O]\ \Delta H(25°) = -1.97 \text{ kcal. per mole}$$

Table I. Heat of Hydrolysis (ΔH_{obsd}) of $SOBr_2$ in Deoxygenated Water

$T = 25.0 \pm 0.1°$ C.

Wt. of Sample, G.	n	ΔH_{obsd}, Kcal. Per Mole	ΔH_f° $SOBr_2$(Liq.), Kcal. Per Mole
1.2546	1381	-29.0_1	−40.2
1.9447	891	-29.0_1	−40.1
1.3087	1322	-28.7_2	−40.5
1.2891	1344	-29.1_4	−40.1

$\Delta H_f^\circ[SOBr_2, liq.] = -40.2 \pm 0.3^a$ kcal. per mole

[a] The error for four observations is taken as the range of the observed data plus the errors on the ancillary data combined as the root of the sum of the squares.