Part I

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Saturation Composition of Steam-Helium-Liquid Water System and P-V-T Data for a Superheated Steam-Helium Mixture

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For 70 years many investigators have measured *P-V-T* data of pure gases, and accurate data are available for most of the common gases over rather wide ranges of temperature and pressure. While such data are of great scientific value, most engineering problems require specific knowledge of gaseous mixtures rather than pure components. By comparison with pure components only a very limited amount of mixture *P-V-T* data has been measured, and, for many mixtures the engineer must attempt to predict the *P-V-T* behavior. Usually mixture *P-V-T* histories are predicted from one of the mixture laws, by using the *P-V-T* data of the pure components. A few rather important generalizations have been made regarding the applicability of mixture laws for several types of gaseous mixtures. No such generalization has been postulated, however, for a mixture at a temperature below the critical temperature of one of the components. The purpose of this investigation was to study such a gaseous mixture—a steam-helium mixture.

Two types of problems are encountered with such mixtures. In many instances conditions of temperature and pressure are such that a two-phase region is present. It is often necessary to attempt to predict the composition of the vapor phase in equilibrium with the liquid phase. Bartlett (*1*) in early work investigated the water-steam-nitrogen and water-steam-hydrogen systems, and compared experimentally determined vapor compositions with compositions calculated from the Poynting relation.

As the first phase of this investigation, the equilibrium composition of the vapor phase was determined for a water-steam-helium system at 300°C., and 2000 pounds per square inch absolute. The experimental technique used was one of dynamic equilibrium. Several methods of predicting the equilibrium vapor composition were attempted. The results of these calculations are compared with the experimental composition.

The second problem is prediction of the *P-V-T* history. The *P-V-T* data for a steam-helium mixture of the determined saturation composition were measured in the superheated region. Several methods of predicting the *P-V-T* history of this mixture were tried and are discussed herein.

APPARATUS

Saturation Study. A schematic diagram of the apparatus used in the saturation study is shown in Figure 1. The high temperature salt bath was especially constructed to contain the saturator and preheating coils. The fluid in the bath was a eutectic mixture of potassium nitrite and sodium nitrite sold commercially by the American Cyanamid Co. under the trade name Aeroheat.

Figure 2 is a sketch of the salt bath and temperature-control circuits. Five 500-watt heaters were controlled manually by a variable transformer to give coarse temperature control. Fine control was effected by a 750-watt U-tube heater controlled by a Brown Electronik potentiometer recorder controller. The temperature of the bath was controlled to within ±0.3°C. at 300°C. The bomb or saturator was a standard Aminco Type 347 stainless steel pressure vessel with a chrome-vanadium head. It had an inner volume of approximately 1730 cc., was $2\frac{9}{16}$ inches in inside diameter, and was 21 inches deep. The top of the pressure vessel had two gas outlets and a thermowell which extended into the center of the vessel. The saturator was filled to a depth of 4 inches with stainless steel packing in the form of $\frac{1}{4}$-inch rings to ensure good gas-liquid contact.

Helium was supplied to the system, as shown in Figure 1, through a line which led into the preheating coil. This line was equipped with a pressure regulator, rupture disk, a pressure gage, a needle valve, and the preheating coils. The preheating coils consisted of 40 feet of stainless 304 tubing, $\frac{1}{4}$ inch in outside diameter and $\frac{3}{32}$ inch in inside diameter.

An orifice immersed in the salt bath controlled the bleed rate of the saturated mixture. The vapor from the saturator was analyzed by condensing the water in an ice trap, in a dry ice trap, and finally by adsorption in a Drierite tube. The remaining helium was metered by a wet-test meter.

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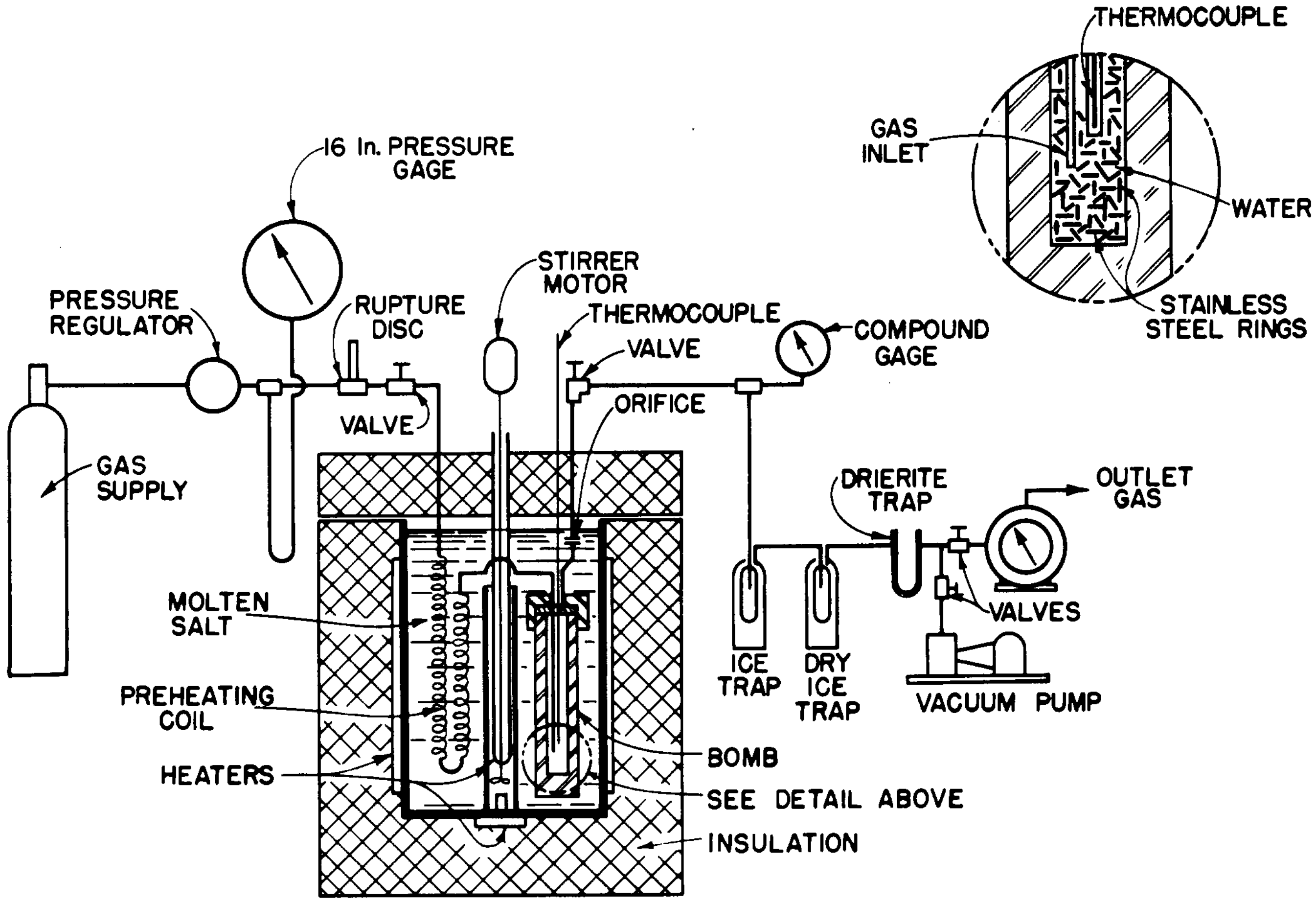

Figure 1. Saturation apparatus and heating bath

Calibration of Instruments. The pressure gage was a 16-inch United States Laboratory test gage, range 0 to 4000 pounds per square inch gage, calibrated periodically on a Crosby dead-weight tester. Its precision was ± 2 pounds per square inch over the range studied.

The temperature in the saturator was measured with a 20-gage Chromel-Alumel thermocouple, calibrated to within ±0.2 °C. by making use of the pressure temperature relationship of saturated steam. The electromotive force output of the couple was measured with a Rubicon Type B high precision potentiometer.

***P-V-T* Apparatus.** Basically the same apparatus was used for the *P-V-T* investigation (Figure 3). The exact volume of the bomb was determined to be 1726.1 cc. at 20 °C. The entire vessel, including sealing gaskets, was made of stainless steel. A three-way valve was used to connect the pressure vessel to the Bourdon-type pressure gage. The tubing from the valve to the gage was mercury-filled. As a result of this, the dead space volume was reduced to 1.4 cc., of which only 1.1 cc. remained out of the salt bath during the experimental runs.

TEST PROCEDURE

Saturation Study. The technique used to determine the saturation composition of the steam-helium-water system was one of dynamic equilibrium.

The saturator was evacuated and half-filled with distilled, degassed water. Then the saturator and preheating coils were lowered into the salt bath, heated, and maintained at 300 °C. for at least 4 hours. Next, helium gas was slowly bled into the bottom of the saturator through the pressure regulator until the total pressure read 2000 pounds per square inch absolute. The saturation system was maintained at 300 °C. for at least 12 hours. Before a run was begun, a volume of vapor greater than the vapor volume of

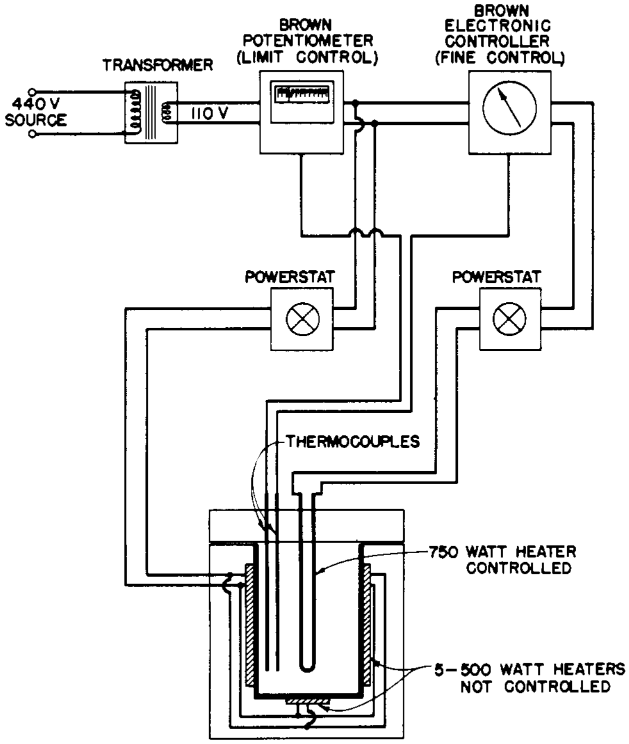

Figure 2. Heater circuits

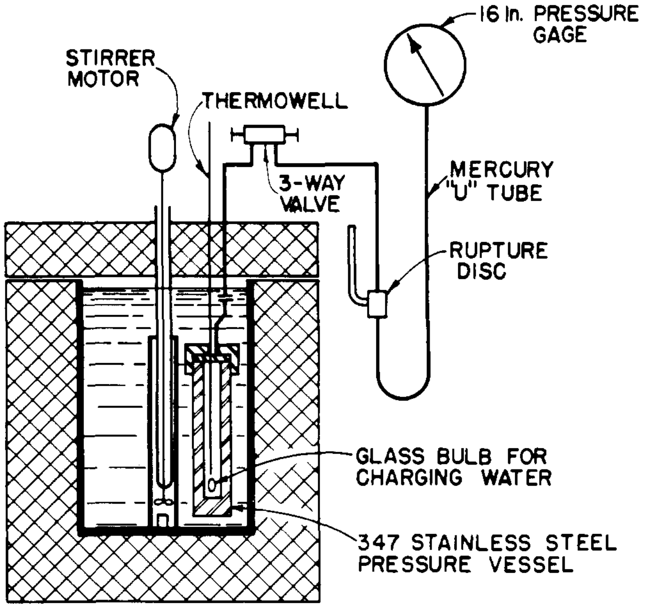

Figure 3. *P-V-T* apparatus

the saturator was bled off. The saturated vapor mixture was expanded through the bath-immersed orifice while a total pressure of 2000 pounds per square inch absolute was maintained by adding helium to the system through the pressure regulator. Bleed rates of approximately 0.1 to 0.5 cubic foot per hour of helium were used to establish the dynamic equilibrium. After expanding through the immersed orifice, the superheated vapor passed through traps and a Drierite tube to remove the water. The water collected was weighed on an analytical balance. The dried helium was then metered by the wet-test meter.

***P-V-T* Study.** Prior to beginning each run, the bomb and tubing were removed from the salt bath. The head was removed from the bomb and all parts were thoroughly cleaned and dried.

Distilled, degassed water was drawn into a tared glass pellet, weighed, and sealed. The volume of the glass pellet was next determined by water displacement. The glass pellet was placed in the bomb and the vessel head was secured.

The bomb was then evacuated and flushed with helium several times. Next the bomb was filled with helium to the desired pressure and was allowed to stand overnight to attain thermal equilibrium. On the following day the pressure and temperature of the bomb were recorded, so that the quantity of helium added could be calculated by making use of *P-V-T* data for helium (*2*).

After checking for leaks, the bomb was lowered into the salt bath and heated until the glass water pellet burst. When all water had vaporized, the bomb was heated well above the saturation point and allowed to stand for several days to ensure that the mixture was uniform throughout. The vessel was then brought to thermal equilibrium at several different temperatures and the pressure and temperature were recorded. A portion of each isochore was reproduced, to ensure that no leaks had developed during the run.

RESULTS

The experimental and calculated results are presented in Tables I to VII and Figure 4.

DISCUSSION OF RESULTS

The equilibrium data measured are presented in Table I. In establishing the dynamic equilibrium, the helium flow rate was varied from 0.164 to 0.560, cubic foot per hour. As the composition of the vapor was shown to be independent of the helium flow rate in the range studied, it was concluded that dynamic equilibrium was attained in all experimental determinations. The mean equilibrium composition of the vapor phase of a water-steam-helium system was determined to be 70.54 mole % steam and 29.46 mole % helium at 300°C. and 2000 pounds per square inch absolute.

In Table II predicted values of the equilibrium vapor composition are presented. Dalton's law used with the *P-V-T* data for the pure components resulted in the closest approximation. In making this calculation the *P-V-T* data of steam presented by Keenan and Keyes (*5*) were used. The *P-V-T* data on helium were taken from a compilation presented by Beattie and Bridgeman (*2*); their original source was the Leiden Laboratory and the Reichsanstalt.

The Poynting relationship integrated by use of the compressibility charts (*3*) used with Dalton's law also gave a close estimate of the composition. In using Dalton's law for this case the *P-V-T* values for steam were estimated from the compressibility chart, as steam does not exist at 300°C. at a vapor pressure of 1298 pounds per square inch absolute. The change in the vapor pressure of the water with total pressure as predicted by the Poynting relationship did not significantly affect the calculated composition. Basically the major correction made by both of these methods of prediction was for deviation of the vapor phase from the ideal gas law. As helium is rather soluble in water (*7*) at these conditions, it is interesting that the equilibrium vapor composition may be reliably predicted by simply correcting for vapor phase deviation from the ideal gas law.

P-V-T DATA

The *P-V-T* data for the steam-helium mixture are presented in Figure 4 and Table III. The data in Figure 3 are presented in the form of isochores.

As rather complete and accurate *P-V-T* data are available for both components of this mixture, attempts were made to predict the mixture *P-V-T* behavior from the constituents' data. The sources for the pure components' *P-V-T* data

Table I. Saturation Vapor Composition of a Steam-Helium-Liquid Water System at 300°C. and 2000 Pounds per Square Inch Absolute

Run No.	Helium Flow Rate, Cu.Ft./Hr., 75°F., 1 Atm.	Saturation Vapor Mixture Composition, Mole %	
		Steam	Helium
1	0.560	70.79	29.21
2	0.507	70.43	29.57
3	0.560	70.70	29.30
4	0.249	70.73	29.27
5	0.263	70.67	29.33
6	0.235	70.17	29.83
7	0.250	70.12	29.88
8	0.330	70.62	29.33
9	0.164	70.60	29.40

Mean saturation vapor mixture composition 70.54 mole % steam-29.46 mole % helium, standard deviation ±0.23%.

Table II. Experimentally Determined and Calculated Saturated Vapor Composition at 300°C. and 2000 Pounds per Square Inch Absolute

Method	Mole % Water	Mole % Helium	Vapor Pressure of Steam, Lb./Sq.Inch Abs.
Experimental	70.54	29.46	....
Dalton's law with perfect gas law	62.3	37.7	1246
Dalton's law with constituents' *P-V-T* data	70.6	29.4	1246
Poynting relationship, perfect gas laws	64.3	35.7	1286
Poynting relationship, compressibility charts for vapor, Dalton's law	71.2	28.8	1298

Table III. *P-V-T* Data for 70.54 Mole % Steam–29.46 Mole % Helium Mixture, Molal Density, Lb. Mole/Cu. Foot

0.07845		0.09835		0.1186		0.1446		0.1624		0.1889		0.2184	
Pressure, (lb./sq. inch abs.)	Temp., °C.	Pressure, (lb./sq. inch abs.)	Temp., °C.	Pressure, (lb./sq. inch abs.)	Temp., °C.	Pressure, (lb./sq. inch abs.)	Temp., °C.	Pressure, (lb./sq. inch abs.)	Temp., °C.	Pressure, (lb./sq. inch abs.)	Temp., °C.	Pressure, (lb./sq. inch abs.)	Temp., °C.
784	290.0	595	222.4	1559	436.5	1872	441.8	2030	421.2	1195	259.7	1820	317.7
829	317.0	592	122.1	1524	421.2	1794	417.3	1998	413.0	1323	297.1	2188	338.4
878	347.6	714	238.3	1338	353.0	1735	398.8	1987	410.0	2017	355.2	2188	337.7
931	382.2	713	238.2	1292	337.1	1686	385.3	1883	380.4	1876	325.8	2188	337.9
979	412.2	892	262.8	1240	316.9	1554	344.8	1834	368.0	1724	300.2	2278	353.7
885	353.7	939	282.5	1196	301.3	1496	326.6	1726	341.0	1631	285.9	2278	353.8
832	316.3	979	310.6	1130	279.1	1450	314.8	1634	318.6	1589	283.9	2353	367.0
835	318.0	1030	321.8	1082	265.0	1362	291.6	1537	294.0	1479	275.7	2408	377.4
817	306.6	1080	343.6	1084	265.7	1295	275.6	1500	285.8	1270	260.0	2406	376.6
784	286.3	1143	372.2	1046	259.8	1191	265.4	1405	277.9	1129	246.8	2404	375.8
752	264.4	1180	389.8	973	253.8	1105	259.4	1340	272.8	970	231.0	2311	359.8
717	250.4	1202	398.4	891	246.0			1285	268.7			2217	343.3
695	241.8	1107	354.3	777	233.2							2209	341.6
681	235.8	1036	322.5	669	219.5							2210	342.1
676	226.4	955	286.7									2116	326.5
544	210.5	765	236.1									2116	326.4
542	210.0	732	238.1									2014	310.8
692	233.8	722	236.8									2014	310.8
724	252.0	730	234.8									2032	312.9
753	266.6	894	261.8									2032	312.9
698	237.8	784	243.5									1810	294.7
721	249.4	730	237.9									1806	294.9
721	249.4											1871	300.4
734	256.5											1875	300.1
												1875	299.4
												1895	301.4
												1995	311.6
												1997	311.6

Table IV. Prediction of Steam-Helium *P-V-T* Data in Superheated Region by Dalton's Law and Constituents' *P-V-T* Data

Molal Density, Lb. Mole/Cu. Ft.	Temperature, °F.														
	580°			600°			700°			800°			900°		
	Pressure, Lb./Sq. Inch Abs.			Pressure, Lb./Sq. Inch Abs.			Pressure, Lb./Sq. Inch Abs.			Pressure, Lb./Sq. Inch Abs.			Pressure, Lb./Sq. Inch Abs.		
	Exptl.	Calcd.	% error	Exptl.	Calcd.	% error	Exptl.	Calcd.	% error	Exptl.	Calcd.	% error	Exptl.	Calcd.	% error
0.07845	813	815	+0.25	830	834	+0.54	915	930	+1.64	996[a]	1018	+2.26	1075[a]	1107	+2.98
0.09835	991	1002	+1.06	1017	1026	+0.93	1142	1150	+0.66	1260[a]	1264	+0.32	1374[a]	1376	+0.15
0.1186	1203	1184	−1.58	1235	1216	−1.54	1388	1368	−1.44	1534	1510	−1.56	1674[a]	1643	−1.85
0.1446	1414	1407	−0.50	1455	1446	−0.62	1644	1638	−0.36	1823[a]	1816	−0.38	1996[a]	1988	−0.41
0.1624	1579	1551	−1.77	1625	1598	−1.66	1846	1816	−1.62	2049[a]	2022	−1.32	2245[a]	2216	−1.24
0.1889	1757	1755	−0.11	1820	1813	−0.38	2086[a]	2076	−0.48	2304[a]	2317	−0.56	2503[a]	2553	−2.00
0.2184	1950	1966	−0.82	2039	2034	−0.24	2376	2348	−1.18						

[a] Extrapolated data.

were the same as were used for the saturation vapor composition predictions. As no accurate helium *P-V-T* data were available above 400 °C., the Beattie-Bridgeman equation of state was used to extrapolate the helium *P-V-T* data to 500 °C.

Methods of prediction tried included (1) Dalton's law of additive pressures; (2) Amagat's law of additive volumes; and (3) the generalized compressibility chart with mixture pseudocritical constants.

As shown in Table IV, Dalton's law of additive pressure used with components' *P-V-T* data predicted the *P-V-T* behavior of the mixture to within ± 1.24% over the entire superheated range investigated.

Some difficulty was encountered in applying Amagat's law of additive volumes, since steam exists only as a liquid at the total mixture pressure over part of the temperature range studied. The *P-V-T* behavior of the mixture was, however, predicted by this method at conditions of temperature and pressure where steam exists as a vapor (Table V). The predicted *P-V-T* values deviated from the experimental data by an average of − 3.21%.

The prediction by the use of the generalized compressibility chart with pseudocritical constants is presented in Table VI. The calculated mixture *P-V-T* behavior deviated ± 1.44% on the average from the experimental *P-V-T* data in the superheated region. Kay's method (*4*) was used to determine the pseudocritical constants. The Newton correction (*6*) was applied for helium in calculating the pseudocritical constants by Kay's method. The compressibility chart presented by Brown (*3*) was used for the calculations.

Table V. Prediction of Steam-Helium *P-V-T* Data in Superheated Region by Amagat's Law and Constituents' *P-V-T* Data

Temp., °F.	Molal Density, Lb./Mole/Cu. Ft.	Pressure, Lb./Sq. Inch Abs.		% Error
		Exptl.	Calcd.	
580	0.1889	....	....	....
	0.09835	991	946	−1.54
600	0.1889	....	....	....
	0.09835	1016	975	−4.04
700	0.1889	2086	1946	−6.71
	0.09835	1141	1111	−2.63
800	0.1889	2304	2217	−3.78
	0.09835	1259	1240	−1.51
900	0.1889	2503	2471	−1.28
	0.09835	1373	1357	−1.17

In addition to the above cited calculations in the superheated region, the saturation conditions, pressure and temperature, were predicted using Dalton's law and constituents' *P-V-T* data. The results of these calculations are

Table VI. Prediction of Steam-Helium *P-V-T* Data in Superheated Region by Generalized Compressibility Charts Used with Pseudocritical Constants

	1.279 (600°F.)					1.399 (700°F.)				
Molal Density, Lb. Mole/ Cu. Ft.	Pressure, (lb./sq. inch abs.)	Reduced pressure	Compressibility Factor		% Deviation	Pressure, (lb./sq. inch abs.)	Reduced pressure	Compressibility Factor		% Deviation
			Exptl.	Charts				Exptl.	Charts	
Reduced Temperature										
0.07845	830	0.3607	0.9305	0.930	0	922	0.4007	0.9445	0.960	+1.7
0.09835	1016	0.4415	0.9085	0.930	+2.4	1141	0.4959	0.9323	0.940	+0.8
0.1186	1236	0.5372	0.9162	0.920	+0.4	1388	0.6032	0.9402	0.930	−1.1
0.1446	1455	0.6323	0.8851	0.910	+2.8	1644	0.7145	0.9138	0.920	+0.6
0.1624	1625	0.7062	0.8798	0.900	+2.3	1844	0.8014	0.9123	0.920	+0.9
0.1889	1820	0.7910	0.8472	0.890	+5.1	2088	0.9074	0.8881	0.910	+2.5
Reduced Temperature										
	1.520 (800°F.)					1.641 (900°F.)				
0.07845	997	0.4333	0.9400	0.060	+2.1	1074	0.4668	0.9384	0.960	+2.3
0.09835	1260	0.5476	0.9476	0.960	+1.3	1374	0.5971	0.9576	0.960	+0.2
0.1186	1535	0.6671	0.9570	0.950	+0.7	1675	0.7279	0.9677	0.969	−0.8
0.1446	1824	0.7927	0.9332	0.950	+1.8	1995	0.8670	0.9459	0.960	+1.5
0.1624	2049	0.8905	0.9330	0.940	+0.8	2245	0.9757	0.9473	0.960	+1.4
0.1889	2303	1.009	0.9016	0.910	+0.9	2503	1.0878	0.9080	0.910	+0.2

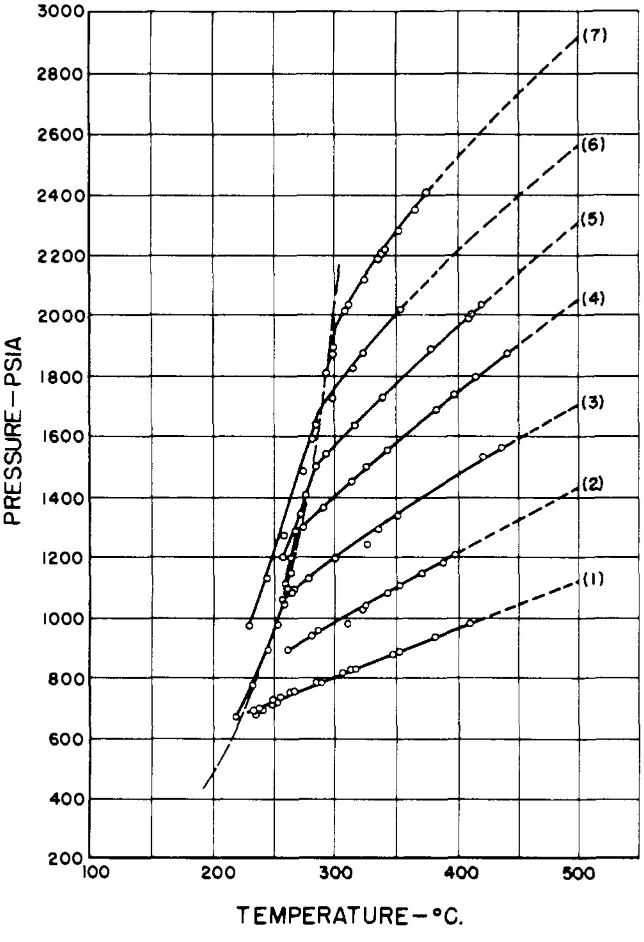

Figure 4 Steam-helium isochores

70.54 mole % steam
29.46 mole % helium

Isochore	Molal Density, Lb. Mole/Cu. Ft.
1	0.07845
2	0.09835
3	0.1186
4	0.1446
5	0.1624
6	0.1889
7	0.2184

Table VII. Prediction of *P-V-T* Data of Steam-Helium Isochores at Saturation Point Using Dalton's Law and *P-V-T* of Pure Constituents

Molal Density, Lb. Mole/Cu. Ft.	Saturation Temp., °F.		% Error (Temp. Basis)	Saturation Pressure, Lb./Sq. Inch Abs.		% Error
	Exptl.	Calcd.		Exptl.	Calcd.	
0.1186	500	502	+0.21	1064	1075	+1.03
0.1446	524	522	−0.20	1284	1301	+1.32
0.1624	540	536	−0.40	1485	1453	−2.15
0.1889	552	552	0.000	1658	1675	+1.02

shown in Table VII. This method predicted the saturation pressure to within ±1.6% on the average.

As this investigation dealt with only one system, no generalizations could be formulated. It has been shown, however, that this mixture containing one component below its critical temperature adequately follows a mixture law.

It may therefore be concluded that the saturation vapor composition of a water-steam-helium system may be predicted from Dalton's law and components' *P-V-T* data. The *P-V-T* behavior of a steam-helium mixture may be estimated by either Dalton's law and components' *P-V-T* data, or by use of the generalized compressibility chart with pseudocritical constants. The applicability of these methods in predicting these properties for other mixtures of this type should be tried as more data become available.

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