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

JAMES A. LUKER, THOMAS GNIEWEK[1], AND CHARLES A. JOHNSON[2]
Syracues University Research Institute, Syracuse University, Syracuse, N. Y.

Because limited *P-V-T* data are available on gaseous mixtures where one or more of the components is below its critical temperature, such a system was investigated: steam-oxygen–liquid water. The saturation vapor composition was determined at 2000 pounds per square inch absolute and 300° C. The *P-V-T* data for a steam-oxygen mixture of the determined equilibrium vapor composition were measured over a pressure range of 1000 to 2000 pounds per square inch absolute and a temperature range of 550° to 950° F.

The experimental procedure for this study was identical to that used in the investigation of the steam-helium-water system (*6*). Saturated vapor compositions were determined by establishing a dynamic equilibrium. All *P-V-T* data were measured as isochores.

Several methods of predicting the equilibrium vapor composition of the saturated mixture and the *P-V-T* behavior of the superheated mixture were tried. Comparisons of experimental data with predicted behavior from mixture laws are presented herein.

RESULTS

The experimental and calculated results are presented in Tables I to VII and Figures 1 and 2.

DISCUSSION OF RESULTS

Saturation Composition. The composition of steam-oxygen vapor in equilibrium with liquid water at 2000 pounds per square inch absolute and 300° C. was determined to be 71.07 mole % steam and 29.93 mole % oxygen (Table 1).

The following methods of predicting this equilibrium vapor composition were tried. (Table II).

1. Dalton's law of additive pressures used with perfect gas law.
2. Dalton's law of additive pressures used with constituents' *P-V-T* data.
3. Mixture and constituents' fugacities determined from the generalized fugacity chart.

As expected, Dalton's law used with the perfect gas law resulted in a large error of prediction. In applying method 2 Dalton's law of additive pressures used with constituents' *P-V-T* data, the *P-V-T* data for steam presented by Keenen and Keyes (*4*) were used. Oxygen *P-V-T* data up to 100° C. were taken from a compilation of data presented by Beattie and Bridgeman (*1*). As no *P-V-T* data for oxygen were available above 100° C., the Beattie-Bridgeman equation was used to estimate the *P-V-T* behavior of oxygen above 100° C. Method 2 predicted the equilibrium vapor composition to within 1.07 mole %. The third method, a use of the generalized fugacity chart, gave the best estimate of the equilibrium vapor composition—within 0.13 mole % of the experimentally determined value.

The composition of the equilibrium vapor was assumed. Using this assumed composition mixture, pseudocritical constants were calculated for the mixture by applying Kay's method (*3*). The fugacity of the mixture, f_m, was then determined from the generalized fugacity chart at the temperature in question and the total pressure. Next the fugacity of each constituent of the vapor, f_{H_2O}, and f_{O_2}, was determined from the generalized compressibility chart at the temperature in question and the total pressure. The composition of the mixture was then calculated from the equality $f_m = f_{H_2O} Y_{H_2O} + f_{O_2} (1 - Y_{H_2O})$, where Y_{H_2O} is equal to the mole fraction of water vapor in the equilibrium mixture. This trial and error procedure was repeated until the assumed and calculated compositions agreed.

Table I. Saturation Vapor Composition of Steam-Oxygen-Liquid Water System at 300° C. (572° F.) and 2000 Pounds per Square Inch Absolute

Run No.	Sampling Time, Hours	Oxygen, Cu. Ft./Hr., 75° F., 1 Atm.	Mixture Composition, Mole %: Oxygen	Mixture Composition, Mole %: Steam
1	4.33	0.108	29.17	70.83
2	0.92	0.553	28.77	71.23
3	1.17	0.437	28.95	71.05
4	1.92	0.251	28.84	71.16

Mean saturation vapor mixture composition 71.07 mole % steam, 28.93 mole % oxygen, standard deviation ± 0.30%.

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

Method	Mole % Steam	Mole % Oxygen
Experimental	71.07	28.93
Dalton's law with perfect gas relationships	62.3	37.7
Dalton's law with constituents' *P-V-T* data	70.0	30.0
Mixture and constituents' fugacities	71.2	28.8

Table III. *P-V-T* Data for 71.07 Mole % Steam-28.93 Mole % Oxygen Mixture

Molal Density, Lb. Mole/Cu. Foot

0.1299		0.1456		0.2160	
Temp., °C.	Pressure, lb./sq. inch abs.	Temp., °C.	Pressure, lb./sq. inch abs.	Temp., °C.	Pressure, lb./sq. inch abs.
274.60	1119	295.53	1441	311.76	1987
271.59	1113	339.10	1555	343.46	2184
279.89	1135	368.16	1648	368.91	2319
294.42	1173	306.92	1448	387.26	2425
299.35	1193	330.89	1525	395.16	2463
341.48	1314	373.65	1669	410.23	2536
367.25	1380	396.42	1734	432.88	2653
399.00	1574	422.78	1823	436.32	2668
425.11	1548	271.42	1253	293.40	1772
438.67	1584	255.12	1049	289.36	1704
410.45	1512	262.38	1142	297.13	1856
367.11	1390	269.50	1228		
330.25	1284	273.65	1284		
296.15	1185	263.78	1163		
266.00	1079	272.46	1278		
275.37	1113				
253.38	953				
247.00	892				
238.11	810				
242.38	887				
268.60	1082				

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[1] Present address, E. I. du Pont de Nemours & Co., Inc., Wilmington, Del.

[2] Present address, Atomic Power Division, Westinghouse Electric Corp., Pittsburgh, Pa.

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

	Molal Density, Lb. Mole/Cu. Foot								
	0.1299			0.1456			0.2160		
	Pressure, Lb./Sq. Inch Abs.			Pressure, Lb./Sq. Inch Abs.			Pressure Lb./Sq. Inch Abs.		
Temp., °F.	Exptl.	Calcd.	% Error	Exptl.	Calcd.	% Error	Exptl.	Calcd.	% Error
580	1208	1199	−0.79	....	....	....	1944	1941	−0.16
600	1214	1213	−0.82	1474	1451	−1.56	2020	2009	−0.54
700	1402	1385	−1.22	1652	1647	−0.30	2326	2325	−0.04
800	1552	1532	−1.31	1828	1828	0.00	2620	2616	−0.15
900	1692	1674	−1.02	2010	2003	−0.35	....	2888	....

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

Temp., °F.	Molal Density, Lb. Mole/ Cu. Ft.	Pressure, Lb./Sq. Inch Abs.		% Error
		Exptl.	Calcd.	
580	0.1299	1208	1132	−6.29
600	0.1456	1474	1341	−9.03
900	0.1299	1692	1632	−1.77
900	0.1456	2010	1965	−2.24

In another investigation (*5,6*) the authors predicted the equilibrium vapor phase composition of a steam-helium-water system at the same conditions to within 0.1 mole % by using Dalton's law and constituents' *P-V-T* data. Although at these conditions oxygen and helium are rather soluble in water (*7*), the equilibrium composition of the vapor may be reliably estimated by proper allowance for vapor phase deviations from the ideal gas law.

P-V-T Data. The *P-V-T* properties of the 71.07 mole % steam–28.93 mole % oxygen mixture were investigated. The *P-V-T* data were measured as pressure-temperature isochores for various molal densities (Table III and Figure 1.) Experimental procedure was identical to that for the steam-helium mixture (*6*). Errors resultant from mixture preparation were negligible. Temperature was controlled to within ± 0.3°C. Pressure measurements were precise to ± 2 pounds per square inch absolute.

Several methods of predicting the experimentally determined *P-V-T* data for this mixture were tried.

1. The perfect gas law.
2. Dalton's law of additive pressure used with constituents' *P-V-T* data.
3. Amagat's law of additive volumes and *P-V-T* data of pure constituents.
4. Generalized compressibility charts using pseudocritical constants for the mixture.

The first method was unsuccessful, as expected, as steam deviates widely from the perfect gas law. In applying Method 2, Dalton's law of additive pressures used with constituents' *P-V-T* data; the *P-V-T* data for the pure constituents were taken from the sources cited in the discussion of saturation vapor composition calculations. Method 2 was successful in predicting the *P-V-T* behavior of the steam-oxygen mixture to within −0.63% over the entire superheated range investigated (Table IV).

The results of the prediction by Amagat's law of additive volumes used with *P-V-T* data of pure constituents are presented in Table V. This mixture law proved to be much less feasible than Dalton's law, as it resulted in an average deviation of −4.83% from the experimental values.

Tabulated in Table VI are predicted values of the compressibility factor for this mixture for isochores one and two, determined by the generalized compressibility chart of Brown (*2*). Pseudocritical constants for the mixture were calculated using Kay's method (*3*). The predicted compressibility factors deviated from the experimentally determined factors by an average of −2.05%. Part of this deviation was undoubtly due to inaccuracies resultant from reading the compressibility chart in the range in question.

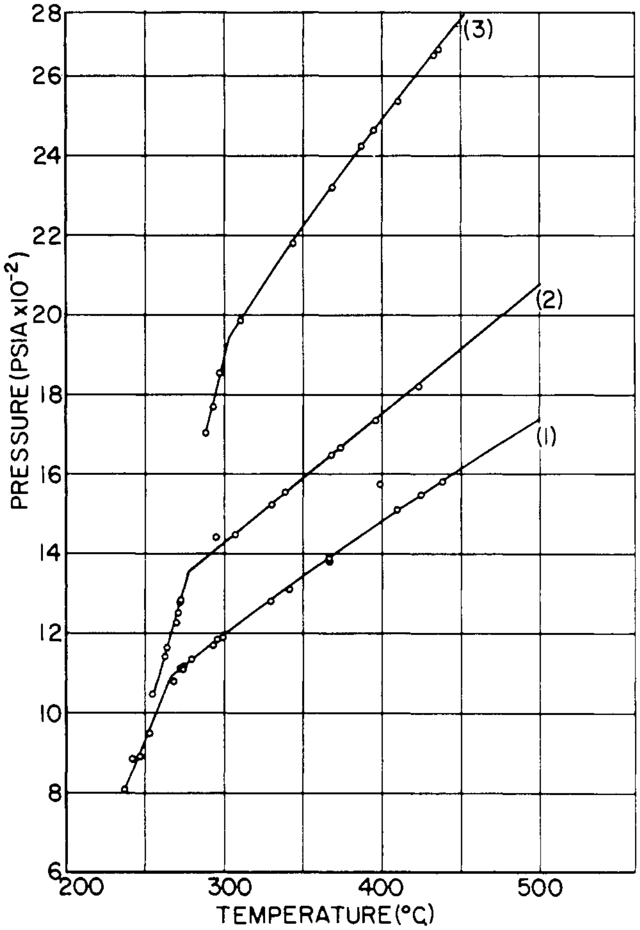

Figure 1. Steam-oxygen isochores

71.07 mole % steam
28.93 mole % oxygen

Isochore	Molal Density, Lb. Mole/Cu. Ft.
1	0.1209
2	0.1456
3	0.2160

Dalton's law and constituents' *P-V-T* data were used to predict the saturation pressure (Table VII). The saturation pressures were predicted to within −2.5% on the average.

As Dalton's law of additive pressures used with the constituents' *P-V-T* data proved to be a very reliable method for predicting the *P-V-T* data for this mixture, it was decided that three experimental isochores provided sufficient data for verification of this technique. In Figure 2 is presented a plot of mixture molal volume *vs.* pressure with constant temperature parameters. This figure was constructed from experimental data and calculated pressures using Method 2.

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

Molal Density, Lb. Mole/ Cu. Ft.	Pressure, Lb./Sq. Inch Abs.	Reduced Pressure	Compressibility Factor		% Deviation
			Exptl.	Charts	
	Reduced Temperature 1.168 (600°F.)				
0.1299	1241	0.4996	0.9025	0.892	−1.11
0.1456	1474	0.5934	0.8901	0.872	−1.32
	Reduced Temperature 1.278 (700°F.)				
0.1299	1403	0.5648	0.9323	0.910	−2.36
0.1456	1621	0.6526	0.8945	0.890	−0.45
	Reduced Temperature 1.389 (800°F.)				
0.1299	1552	0.6248	0.9495	0.920	−3.05
0.1456	1831	0.7371	0.9447	0.911	−3.60
	Reduced Temperature 1.498 (900°F.)				
0.1299	1692	0.6812	0.9590	0.939	−2.09
0.1456	2011	0.8096	0.9465	0.921	−2.44

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

Molal Density, Lb. Mole/ Cu. Ft.	Saturation Temp.,		% Error	Saturation Pressure, Lb./Sq. Inch Abs.		% Error
	Exptl.	Calcd.		Exptl.	Calcd.	
0.1299	506	511	+0.52	1092	1075	−1.55
0.1456	526	531	+0.51	1360	1302	−4.26
0.2160	578	567	−0.43	1940	1907	−1.70

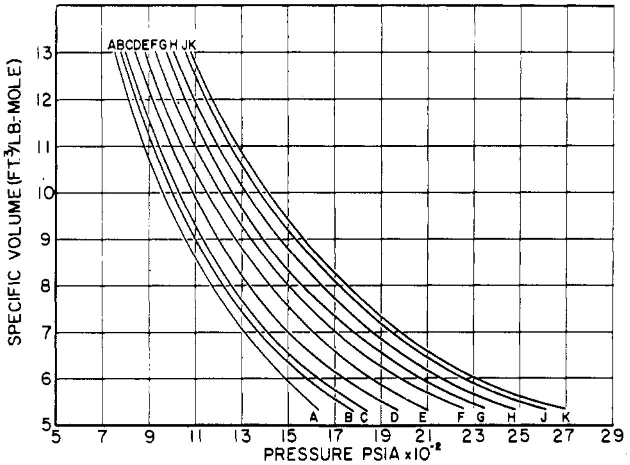

Figure 2. Steam-oxygen isotherms calculated using Dalton's Law

71.07 mole % steam
28.93 mole % oxygen

Curve	Temp., °F.
AA	550
BB	580
CC	600
DD	650
EE	700
FF	750
GG	800
HH	850
JJ	900
KK	930

It may be concluded that this mixture containing one component below its critical temperature adequately follows Dalton's law. It has been shown (6) that the steam-helium mixture was also adequately defined by Dalton's law. As the data presented in this and the other article (6) on the steam-helium mixture constitute the only data available for such mixtures, no generalizations regarding the applicability of Dalton's law for this type of mixture can be made. As more mixture *P-V-T* data are made available, the validity of using Dalton's law for predicting the saturation vapor composition and the *P-V-T* behavior for mixtures of this type should be tested.

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