Enthalpy and Heat Capacity of Steam-Helium and Steam-Oxygen Mixtures

JAMES A. LUKER, THOMAS GNIEWEK,[1] AND STANLEY A. MOSIER[2]
Syracuse University Research Institute, Syracuse University, Syracuse, N. Y.

In making design calculations for high pressure systems, the practicing engineer is often concerned with the transfer of heat. In many instances heat effects must be evaluated in high pressure flow systems which involve mixtures of gases. Although thermodynamic property charts or tables are available for some pure gases, very few thermodynamic properties have been established for gaseous mixtures at elevated pressures.

Enthalpy and heat capacity are the two thermodynamic properties most frequently used in engineering calculations. To calculate rigorously the effect of pressure on the enthalpy and heat capacity of a gaseous mixture or a pure component requires very accurate *P-V-T* data. Because such data are often unavailable, approximate methods must be used.

The purpose of this investigation was to estimate the enthalpy and heat capacity of steam-helium and steam-oxygen mixtures at elevated temperatures and pressures.

The authors have presented *P-V-T* data for steam-helium and steam-oxygen mixtures (*6,7*). Unfortunately, the *P-V-T* behavior of these mixtures was not sufficiently established to permit rigorous calculation of the thermodynamic properties over the entire range investigated.

Sufficient *P-V-T* data were available for a rigorous determination of the effect of pressure on the enthalpy of the steam-helium mixture at 650°F. This calculation was made and the results are presented herein.

In the analysis of the *P-V-T* data for these two mixtures, the authors showed that the *P-V-T* behavior of these mixtures could be reliably predicted by use of Dalton's law and *P-V-T* data on pure components. The steam-helium *P-V-T* behavior was predicted to within ± 1.24%; the steam-oxygen *P-V-T* behavior, to within − 0.63%. The success of Dalton's law in predicting these *P-V-T* histories seems to indicate that each component acts independently in these mixtures. Thus, the enthalpies and heat capacities may also be calculated from the thermodynamic properties of the pure components at their respective partial pressures for the temperature in question.

To test the validity of the use of Dalton's law in calculating the thermodynamic properties of these mixtures, the effect of pressure on the enthalpy of the steam-helium mixture at 650°F. was calculated by this technique. From a comparison of the results of this calculation to enthalpy change predicted from the *P-V-T* data for this mixture it was concluded that Dalton's law and constituent thermodynamic properties may be used to predict the thermodynamic properties of these mixtures. Using this technique the enthalpy and heat capacity of these mixtures were calculated.

Presented herein are the enthalpies and heat capacities of a 70.54 mole % steam-29.46 mole % helium mixture and a 71.07 mole % steam-28.93 mole % oxygen mixture. These properties are presented as a function of temperature over the range 550° to 950°F. for isobars from 1000 to 2000 pounds per square inch absolute.

CALCULATIONS

Effect of Pressure on Enthalpy of Steam-Helium Mixture Using Mixture *P-V-T* Data. A complete set of thermodynamic properties for a single-phase system may be calculated from the *P-V-T* data and heat capacity data at one pressure. However, *P-V-T* data must be very accurate, to make this computation practical. For the mixture in question the *P-V-T* data were not accurate enough for the calculation of thermodynamic properties over the entire range investigated, but it was deemed feasible to calculate the change of enthalpy with pressure at one temperature (650°F.).

The basic thermodynamic relation used was:

$$\Delta H_T = \Delta E - \Delta PV$$

$$\Delta H_T = J \int_{V_1}^{V_2} \left[T \left(\frac{\partial P}{\partial T} \right)_V - P \right] dV + J(P_2 V_2 - P_1 V_1) \qquad (1)$$

To evaluate each term in Equation 1 as accurately as possible, empirical equations were fitted to the experimental *P-V-T* isochores (*6*) using linear or curve-linear regression (*3*). The equations developed were as follows, where P = pressure in pounds per square inch absolute and t = temperature in °C.

Isochore 1. Molal volume, 12.75 cu.ft./lb. mole
$P = 854.8 + 1.526\ (t - 331.4)$. Temperature range, 264° to 412°C.

Isochore 2. Molal volume, 10.17 cu.ft./lb.mole
$P = 1100 + 2.031\ (t - 352.5)$. Temperature range, 286° to 399°C.

Isochore 3. Molal volume, 8.532 cu.ft./lb.mole
$P = 1318 + 2.736\ (t - 345.9)$. Temperature range, 301° to 421°C.

Isochore 4. Molal volume, 6.916 cu.ft./lb.mole
$P = 4.446 \times 10^3 + 6.096 \times 10\,t - 2.625 \times 10^{-1} t^2 + 5.412 \times 10^{-4} t^3 - 4.238 \times 10^{-7} t^4$. Temperature range, 291° to 386°C.

Isochore 5. Molal volume, 6.158 cu.ft./lb.mole
$P = -1.558 \times 10^4 + 1.829 \times 10^2 t - 7.548 \times 10^{-1} t^2 + 1.419 \times 10^{-3} t^3 - 1.003 \times 10^{-6} t^4$. Temperature range, 318° to 410°C.

Isochore 6. Molal volume, 5.294 cu.ft./lb.mole
$P = 1.911 \times 10^3 - 1.811 \times 10\,t + 9.332 \times 10^{-2} t^2 - 1.168 \times 10^{-4} t^3$. Temperature range, 285° to 355°C.

Isochore 7. Molal volume, 4.579 cu.ft./lb.mole
$P = 3.998 \times 10^3 - 6.208 \times 10\,t + 3.917 \times 10^{-1} t^2 - 9.272 \times 10^{-4} t^3 + 7.830 \times 10^{-7} t^4$. Temperature range, 310° to 376°C.

The above empirical equations represent the experimental *P-V-T* data of the steam-helium mixture to within the experimental precision of the investigation (± 2 pounds per square inch). These equations were used to calculate the terms in the basic thermodynamic equation cited above. By algebraically solving for the $\frac{(\partial P)}{(\partial T)_V}$, the inherent error in the derivative was minimized. Tabulated in Table I are

---

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

[2] Present address, Pratt & Whitney Aircraft, East Hartford, Conn.

Table I. Parameters for Calculating Effect of Pressure on Enthalpy of Steam-Helium Mixture

[Temperature 343.33 °C. (650 °F.)]

Isochore No.	Molal Volume, Cu. Ft./Lb. Mole	Pressure, Lb./Sq. Inch Abs.	$\frac{\partial P}{\partial T_V}$, Lb./Sq. Inch Abs./°K.	$T\frac{\partial P}{\partial T_V}$	$T\frac{\partial P}{\partial T_V} - P$	PV
1	12.75	872	1.526	941	69	11,120
2	10.17	1082	2.031	1252	170	11,000
3	8.432	1311	2.736	1687	376	11,050
4	6.916	1552	3.500	2158	606	10,730
5	6.158	1733	4.050	2497	764	10,410
6	5.294	1966	4.660	2873	907	10,410
7	4.579	2219	5.770	3557	1338	10,160

Table II. Effect of Pressure on Enthalpy of Steam-Helium Mixture

(Datum plane. 872 lb./sq. inch abs. and 650 °F.)

V, Cu. Ft./Lb. Mole	P, Lb./Sq. Inch Abs.	Area from $T\frac{\partial P}{\partial T_V} - P$ vs. V, Lb./Sq. Inch Abs.-Cu. Ft./Lb. Mole	Cumulative Area, Lb./Sq. Inch Abs.-Cu. Ft./Lb. Mole	Internal Energy Change, B.t.u./Lb. Mole	ΔPV, Lb./Sq. Inch Abs.-Cu. Ft./Lb. Mole	ΔPV, B.t.u./Lb. Mole	ΔH_T, B.t.u./Lb. Mole
12.75	872	...	...	...	...	...	...
10.17	1082	−273	−273	−51	−120	−22	−73
8.432	1311	−458	−731	−135	−50	−9	−144
6.916	1552	−745	−1477	−273	−390	−72	−345
6.158	1733	−515	−1992	−368	−450	−83	−451
5.294	1966	−731	−2723	−504	−710	−131	−635
4.579	2219	−737	−3460	−640	−960	−178	−818

calculated parameters which were used in completing this computation. In Table II the results of graphically integrating equation one are tabulated, with the change of enthalpy with pressure.

Enthalpy by Dalton's Law and Constituent Thermodynamic Data. Sample calculation shown for 70.54 mole % steam-29.46 mole % helium mixture at 1000 lb./sq. inch abs. and temperature of 650 °F. Basis. One mole of mixture.

1. Assume partial pressure of steam	682 lb./sq. inch abs.
Specific volume steam at 682 lb./sq. inch abs. and 650 °F. (*5*)	0.8806 cu. ft.
Mixture molal volume (0.8806)(18.016)(0.7054)	11.19 cu. ft.
Helium molal volume $\frac{11.19}{0.2946} =$	37.9 cu. ft.
Partial pressure of helium at 37.9 cu. ft./lb. mole and 650 °F. (*1*)	317.4 lb./sq. inch abs.
Total pressure = 682 + 317 =	999 lb./sq. inch abs.
2. Enthalpy of steam at 0.8806 cu.ft./lb. and 650 °F. (*5*)	1315.4 B.t.u./lb.
Enthalpy of steam for 1 lb. mole of mixture (1315.4)(18.016)(0.7054) =	16,717 B.t.u.
3. Calculation of helium enthalpy at 317 lb./sq. inch abs. and 650 °F.	
Datum plane chosen as 32 °F. and 4.4 lb./sq. inch abs.	
Mean heat capacity of helium between 32° and 650 °F. (*4*)	4.965 B.t.u./lb. mole °F.
Helium enthalpy at 650 °F. and 4.4 lb./sq. inch abs. (4.965)(650−32)(0.2946) =	904 B.t.u./lb. mole mixture

Helium enthalpy variation with pressure.

$$\frac{\partial H}{\partial P}_T = \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right]$$

$$\Delta H = \int_{4.4}^{317} V dP - 1100 \int_{4.4}^{317} \left(\frac{\partial V}{\partial T}\right)_P dP$$

Both of the above integrals were evaluated using the Beattie-Bridgeman equation of state (2)

ΔH = 3.59 B.t.u./lb. mole helium

Enthalpy change for 0.2946 lb. mole helium (3.59)(0.2946) =	1.06 B.t.u./lb. mole mixture
Total enthalpy change for helium = 904 + 1.06 =	905 B.t.u./lb. mole mixture

Assuming no heat of mixing the steam and helium vapors.

Total enthalpy change for mixture = enthalpy of steam + enthalpy of helium

Above 32 °F. liquid water = 16,717 + 905

4.4 lb./sq. inch abs. helium datum plane = 17,622 B.t.u. per lb. mole mixture

DISCUSSION OF RESULTS

Enthalpy. The effect of pressure on the enthalpy of a steam-helium mixture is shown in Figure 1, where the change in enthalpy with pressure at 650 °F. calculated from the steam-helium *P-V-T* data is presented for a pressure range of 872 to 2219 pounds per square inch absolute. From the smooth curve through these data, the change of enthalpy with pressure was calculated for a datum plane of 1000 pounds per square inch absolute and 650 °F. In Table III the changes in enthalpy with pressure calculated from mixture *P-V-T* data and Dalton's law and component enthalpy

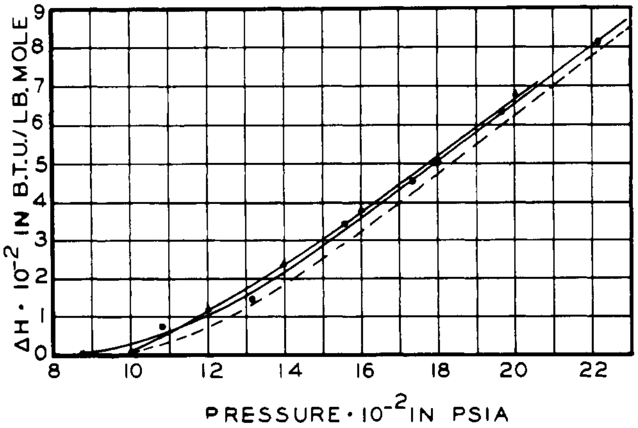

Figure 1. Change of enthalphy with pressure at 650° F.

● Steam-helium mixture based on P-V-T data
Datum plane 872 lb./sq. inch abs.

▲ Steam-helium mixture based on Dalton's law
Datum plane 1000 lb./sq. inch abs.

- - - Smoothed steam-helium data based on P-V-T data
Datum plane 1000 lb./sq. inch abs.

Table III. Effect of Pressure on Enthalpy of Steam-Helium Mixture

(Datum plane. 1000 lb./sq. inch abs. and 650° F.)

Pressure, Lb./Sq. Inch Abs.	ΔH Calcd., B.t.u./Lb. Mole, From P-V-T data	ΔH Calcd., B.t.u./Lb. Mole, From Dalton's law	Deviation, ΔH Dalton's Law-$\Delta H_{P\text{-}V\text{-}T}$, B.t.u./Lb. Mole	% Deviation, Basis $\Delta H_{P\text{-}V\text{-}T}$
1000	...	...	...	...
1200	−70	−122	−52	+74.3
1400	−189	−248	−59	+31.2
1600	−330	−379	−49	+14.8
1800	−480	−511	−31	+6.5
2000	−627	−682	−55	+8.8
		Mean deviation =	−49	

data are compared. The maximum deviation between the ΔH's calculated by the two methods was −59 B.t.u., and the mean deviation was −49 B.t.u. These ΔH's yielded the same shaped curves when plotted against pressure in Figure 1. While there is a constant error between the two methods of calculation, it was concluded that the comparison justifies the use of Dalton's law and component enthalpy data, as a mean difference of −49 B.t.u. will not significantly affect the calculation of the total enthalpy of the mixture.

Thus, the enthalpies of the steam-helium and steam-oxygen mixture were calculated from Dalton's law and constituent thermodynamic properties. The sources of the oxygen thermodynamic data were:

1. P-V-T data were estimated from Beattie-Bridgeman equation (*2*).
2. Heat capacity of oxygen was taken from Keenan and Kaye (*4*).

The molal enthalpy of the 70.54 mole % steam-29.46 mole % helium mixture and the molal enthalpy of the 71.07 mole % steam-28.93 mole % oxygen mixture are presented as a function of temperature in Figure 2. Enthalpies are presented in Table IV.

Heat Capacity. The heat capacity of these mixtures was first calculated by graphical differentiation of the enthalpy-temperature isobars. As these enthalpy isobars had only slight curvature except as saturation was approached, it was difficult to differentiate these curves accurately. Thus, heat capacities were also calculated from Dalton's law and component heat capacity data.

Table IV. Molal Enthalpy Calculated Using Dalton's Law and Constituent Thermodynamic Properties

Temp., °F.	Enthalpy, B.t.u./Lb. Mole of Mixture, 1000 lb./sq. inch abs.	1200 lb./sq. inch abs.	1400 lb./sq. inch abs.	1600 lb./sq. inch abs.	1800 lb./sq. inch abs.	2000 lb./sq. inch abs.
			Steam-Helium Mixture			
550	16,585	16,435	....	....	....	....
580	16,910	16,750	16,605	16,410	16,125	15,860
600	17,134	17,978	16,870	16,720	16,452	16,210
650	17,622	17,500	17,374	17,243	17,111	16,940
700	18,100	17,991	17,885	17,771	17,660	17,548
800	18,970	18,890	18,811	18,743	18,650	18,581
850	19,400	19,328	19,263	19,192	19,114	19,050
900	19,824	19,758	19,705	19,640	19,577	19,517
950	20,260	20,197	20,144	20,091	20,034	19,963
			Steam-Oxygen Mixture			
550	17,080	16,871	16,654	....	....	....
600	17,666	17,492	17,337	17,158	16,966	16,835
700	18,716	18,611	18,507	18,387	18,279	18,151
800	19,717	19,632	19,557	19,472	19,392	19,292
900	20,686	20,614	20,558	20,481	20,427	20,366

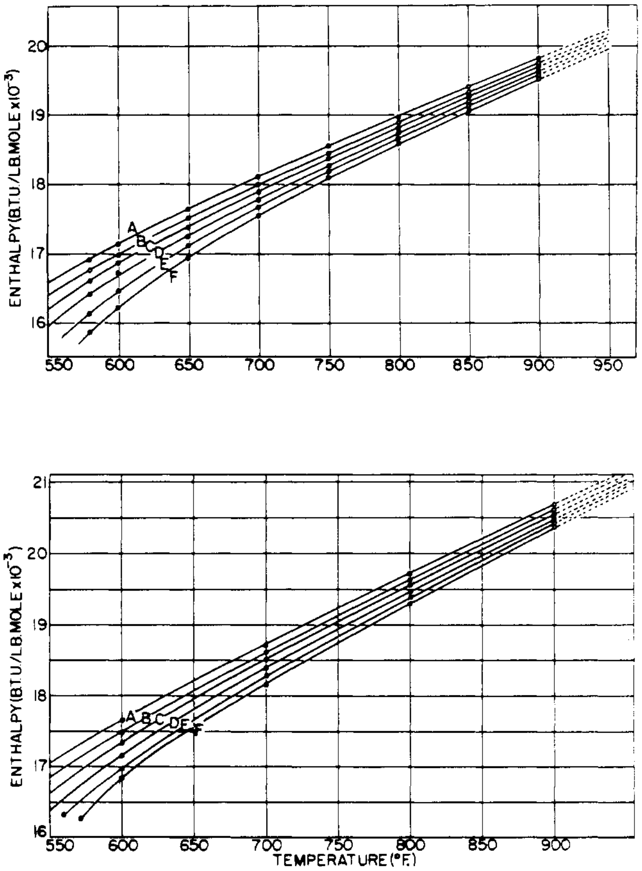

Figure 2. Enthalpy-temperature isobars

Basis Dalton's law

A. 1000 lb./sq. inch abs.
B. 1200 lb./sq. inch abs.
C. 1400 lb./sq. inch abs.
D. 1600 lb./sq. inch abs.
E. 1800 lb./sq. inch abs.
F. 2000 lb./sq. inch abs.

Upper. 70.54 mole % steam
29.46 mole % helium
Lower. 71.07 mole % steam
28.93 mole % oxygen

Table V. Molal Heat Capacity Calculated by Graphical Differentiation

	Heat Capacity, B.t.u./Lb. Mole, °F.					
Temp., °F.	1000 lb./sq. inch abs.	1200 lb./sq. inch abs.	1400 lb./sq. inch abs.	1600 lb./sq. inch abs.	1800 lb./sq. inch abs.	2000 lb./sq. inch abs.
			Steam-Helium Mixture (Figure 2, upper)			
506 (satn.)	11.8	...	...	...	...	...
520 (satn.)	...	12.4	...	...	...	...
532 (satn.)	...	...	13.0	...	...	...
552 (satn.)	...	...	...	14.5	...	...
563 (satn.)	...	...	...	...	16.1	...
572 (satn.)	...	...	...	...	...	...
600	10.1	11.0	11.6	13.2	14.3	16.0
650	9.2	9.4	9.8	10.4	12.2	13.3
700	8.9	9.1	9.4	9.7	9.8	11.1
750	8.4	8.9	9.1	9.6	9.7	10.2
800	8.2	8.6	8.8	9.0	9.3	10.0
850	8.2	8.6	8.8	9.0	9.1	9.1
900	8.2	8.4	8.6	8.7	8.8	8.9
			Steam-Oxygen Mixture (Figure 2, lower)			
498 (satn.)	15.1	...	...	...	...	...
517 (satn.)	...	15.6	...	...	...	...
534 (satn.)	...	...	16.3	...	...	...
549 (satn.)	...	...	...	17.1	...	...
560 (satn.)	...	...	...	...	18.3	...
572 (satn.)	...	...	...	...	...	20.8
600	11.1	12.0	12.7	13.7	14.8	17.1
650	10.5	11.0	11.1	12.4	12.7	13.1
700	9.6	10.6	10.5	11.1	11.4	12.2
750	9.4	9.9	10.2	10.6	10.8	11.6
800	9.4	9.7	10.1	10.4	10.3	11.0
850	9.3	9.6	10.0	9.8	10.3	10.5
900	9.2	9.4	9.6	9.6	10.2	10.3

Table VI. Molal Heat Capacity Calculated Using Dalton's Law and Constituent Heat Capacity Data

	Mixture Heat Capacity in B.T.U./Lb. Mole, °F, for Isobars of					
Temp., °F.	1000 lb./sq. inch abs.	1200 lb./sq. inch abs.	1400 lb./sq. inch abs.	1600 lb./sq. inch abs.	1800 lb./sq. inch abs.	2000 lb./sq. inch abs.
			Steam-Helium Mixture			
492 (satn.)	12.1	...	...	...	...	...
515 (satn.)	...	12.6	...	...	...	...
534 (satn.)	...	...	13.6	...	...	...
550 (satn.)	...	...	...	15.4	...	...
561 (satn.)	...	...	...	...	17.0	...
572 (satn.)	...	...	...	...	...	...
600	10.3	11.2	11.9	13.4	14.7	16.6
700	9.2	9.6	10.2	10.5	11.1	11.6
800	8.7	8.9	9.2	9.4	9.7	9.8
900	8.5	8.7	8.8	8.9	9.1	9.2
			Steam-Oxygen Mixture			
498 (satn.)	14.9	...	...	...	...	...
517 (satn.)	...	16.0	...	...	...	...
534 (satn.)	...	...	16.4	...	...	...
549 (satn.)	...	...	...	18.1	...	...
560 (satn.)	...	...	...	...	18.6	...
572 (satn.)	...	...	...	...	...	20.8
550	11.7	13.2	14.7	...	...	...
600	10.6	11.5	12.5	13.7	14.7	17.4
700	9.4	9.6	9.9	10.8	11.4	11.7
800	8.8	9.3	9.5	9.7	10.1	10.2
900	8.8	9.0	9.2	9.3	9.4	9.6

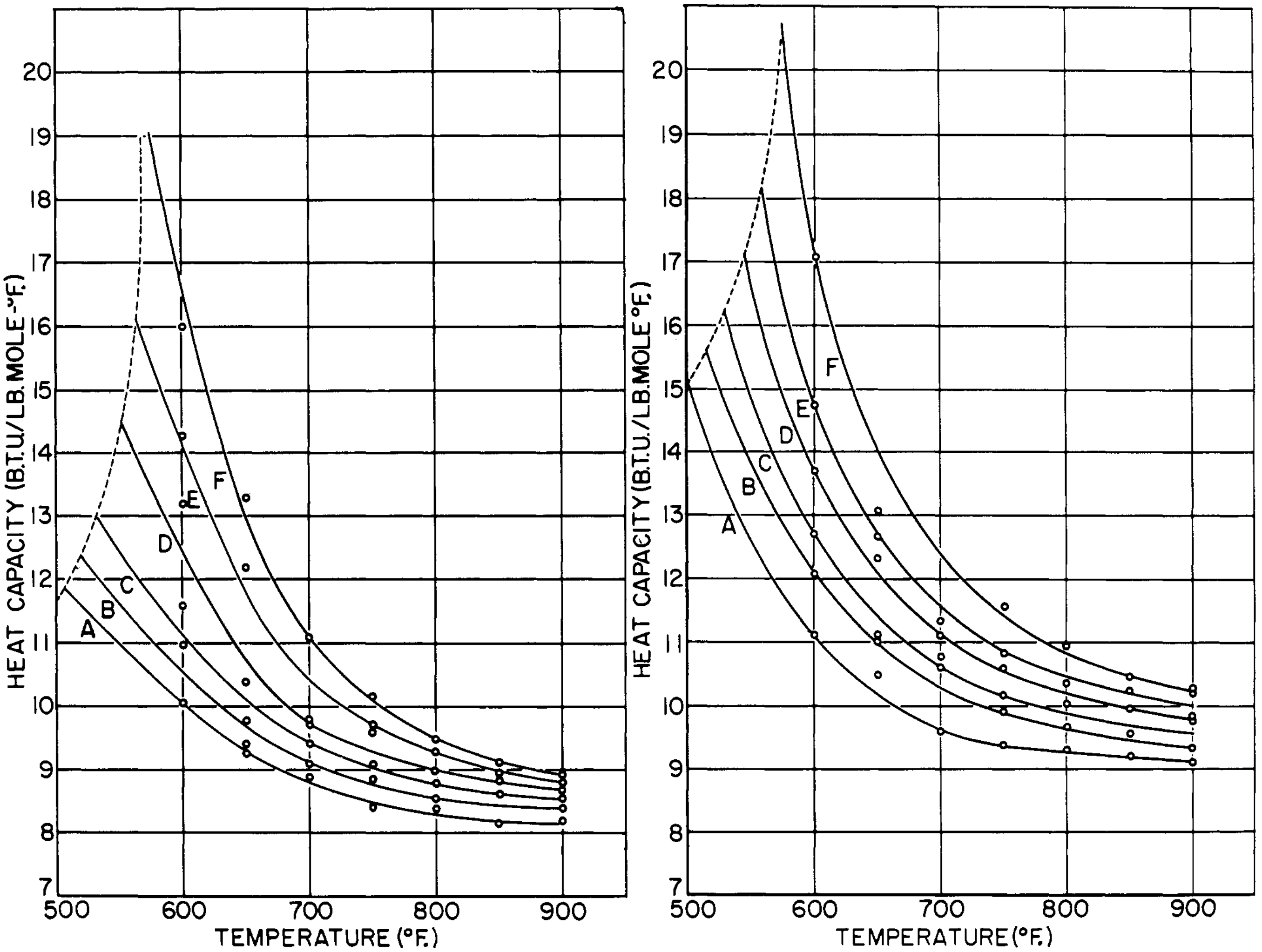

Figure 3. Heat capacity–temperature isobars

A. 1000 lb./sq. inch abs.
B. 1200 lb./sq. inch abs.
C. 1400 lb./sq. inch abs.
D. 1600 lb./sq. inch abs.
E. 1800 lb./sq. inch abs.
F. 2000 lb./sq. inch abs.

Left. Steam-helium mixture
Basis. Graphical differentiation Figure 2, upper
Right. Steam-oxygen mixture
Basis. Graphical differentiation Figure 2, lower

Calculation of Mixture Molal Heat Capacity Using Dalton's Law. Sample calculation shown for 70.54 mole % steam–29.46 mole % helium mixture are total pressure of 1000 lb./sq. inch abs. and temperature of 600 °F.

Partial pressure of steam	680 lb./sq. inch abs.
Heat capacity of steam at 680 lb./sq. inch abs. and 600 °F. (*5*)	0.691 B.t.u. per lb., °F.
Partial heat capacity of mixture due to steam (0.691) (18.016) (0.7054) =	$\frac{\text{8.79 B.t.u.}}{\text{lb. mole mix.}}$
Partial pressure of helium	320 lb./sq. inch abs.
Heat capacity of helium at 4.4 lb./sq. inch abs. and 600 °F. (*4*).	$\frac{\text{4.965 B.t.u.}}{\text{lb. mole °F.}}$

Variation of helium heat capacity with pressure

$$\frac{\partial C_P}{\partial P_T} = -T\frac{\partial^2 V}{\partial T_P^2}$$

$$\Delta C_P = -T\int_{4.4}^{320} \frac{\partial^2 V}{\partial T_P^2}\, dP$$

This integral was evaluated using the Beattie-Bridgeman equation of state. Effect of pressure on heat capacity of helium was negligible.

Partial heat capacity of steam = 8.79 B.t.u./lb. mole mix. °F.
Partial heat capacity of helium = 1.50 B.t.u./lb. mole mix. °F.
Heat capacity of the mixture = 10.29 or 10.3 B.t.u./lb. mole mix. °F.

The molal heat capacities of these mixtures are tabulated in Tables V and VI and presented graphically as isobars in Figures 3 and 4. In Table VII the molal heat capacities calculated by the two methods are compared. The maximum deviation was 8.8%; the average deviation was well within 5%. These deviations probably resulted to a great extent from inherent errors in differentiating the enthalpy-temperature isobars.

As the heat capacities calculated from Dalton's law shown in Figure 4 resulted in less deviation from smooth curves than the heat capacities calculated by graphical differentiation shown in Figure 3, the use of Dalton's law with constituent heat capacity data seems to be the best method of calculation.

Although the exact accuracy of these calculated thermodynamic properties is difficult to ascertain, the properties as presented should be of value in engineering usage.

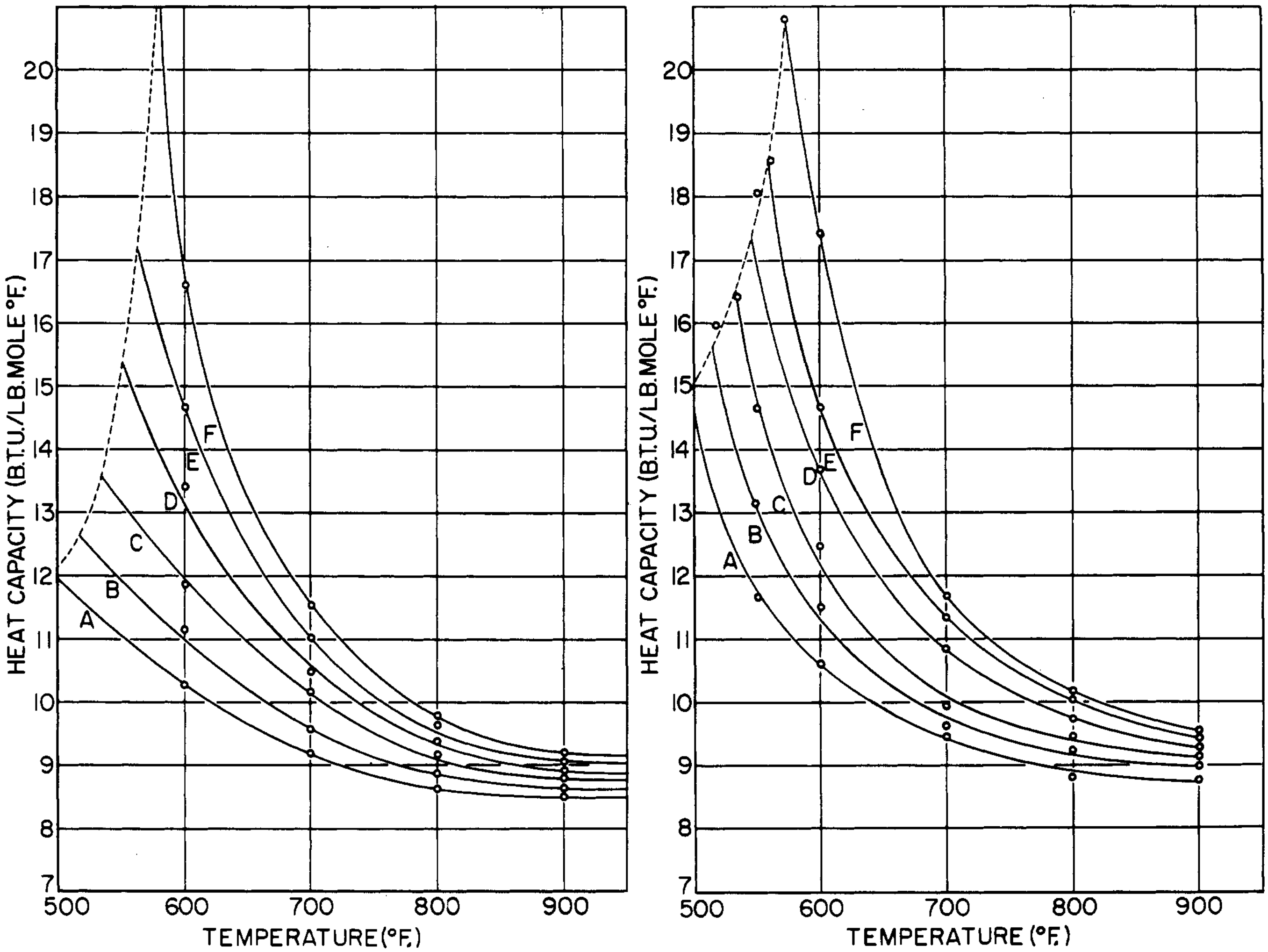

Figure 4. Heat capacity-temperature isobars

Basis. Dalton's law

A. 1000 lb./sq. inch abs.
B. 1200 lb./sq. inch abs.
C. 1400 lb./sq. inch abs.
D. 1600 lb./sq. inch abs.
E. 1800 lb./sq. inch abs.
F. 2000 lb./sq. inch abs.

Left. Steam-helium mixture
Right. Steam-oxygen mixture

Table VII. Comparison of Molal Heat Capacities Calculated by Dalton's Law and Heat Capacities of Constituents with Molal Heat Capacity Calculated by Graphical Differentiation

	1000 Lb./Sq. Inch Abs.			1200 Lb./Sq. Inch Abs.			1400 Lb./Sq. Inch Abs.			1600 Lb./Sq. Inch Abs.			1800 Lb./Sq. Inch Abs.			2000 Lb./Sq. Inch Abs.		
Temp., °F.	Dalton's law	Graph. diff.	% dev.	Dalton's law	Graph. diff.	% dev.	Dalton's law	Graph. diff.	% dev.	Dalton's law	Graph. diff.	% dev.	Dalton's law	Graph. diff.	% dev.	Dalton's law	Graph. diff.	% dev.
									Steam-Helium Mixture									
Satn.	12.0	11.8	1.7	12.6	12.4	2.4	13.6	12.9	5.2	15.4	14.5	6.7	17.1	16.1	6.2	...	...	...
600	10.3	10.0	2.4	11.0	10.6	4.5	12.0	11.2	6.6	13.2	12.4	6.5	14.7	14.1	4.0	16.8	16.6	1.0
650	9.7	9.3	4.1	10.2	9.7	5.8	11.0	10.1	8.4	11.7	10.7	8.8	12.5	11.8	5.9	13.1	13.0	0.9
700	9.2	8.8	4.3	9.6	9.1	5.3	10.2	9.4	7.6	10.6	9.8	8.7	11.1	10.4	6.1	11.5	11.1	3.3
750	8.9	8.5	4.4	9.1	8.8	4.5	9.5	9.0	5.4	9.9	9.3	6.4	10.3	9.7	5.6	10.5	10.1	3.3
800	8.7	8.3	4.5	8.9	8.6	4.0	9.1	8.8	4.0	9.4	9.0	4.1	9.6	9.3	3.3	9.8	9.5	3.3
850	8.6	8.2	4.5	8.8	8.4	3.8	8.9	8.6	3.4	9.1	8.8	3.1	9.2	9.0	2.8	9.4	9.1	2.8
900	8.5	8.1	4.8	8.7	8.4	3.4	8.8	8.6	3.3	9.0	8.7	3.0	9.1	8.8	3.2	9.2	8.9	3.6
									Steam-Oxygen Mixture									
Satn.	15.1	15.1	0.0	15.6	15.6	0.0	16.6	16.3	1.7	17.4	17.1	1.7	18.6	18.3	1.5	20.8	20.8	0.0
600	11.8	11.1	5.3	13.0	12.0	8.3	12.2	12.7	3.6	13.7	13.7	0.0	14.7	14.7	0.0	16.8	17.1	2.2
650	10.6	10.4	1.5	11.3	11.0	2.9	10.9	11.5	5.5	11.9	12.2	1.7	12.6	12.9	2.2	13.2	13.8	4.3
700	9.9	9.7	2.1	10.3	10.3	0.3	10.1	10.7	5.6	10.8	11.2	2.8	11.4	11.7	2.6	11.7	12.3	5.1
750	9.4	9.4	0.0	9.8	9.9	2.5	9.7	10.2	5.1	10.2	10.6	3.2	10.6	10.9	2.7	10.8	11.4	4.5
800	8.9	9.3	4.3	9.4	9.7	2.9	9.4	9.9	5.3	9.8	10.2	4.7	10.1	10.5	3.8	10.3	10.9	5.4
850	8.8	9.2	4.4	9.2	9.5	3.4	9.2	9.7	5.1	9.5	10.0	5.0	9.7	10.2	4.9	9.9	10.5	6.2
900	8.8	9.2	4.4	9.0	9.4	4.1	9.2	9.6	4.8	9.3	9.8	5.1	9.5	10.0	5.1	9.6	10.3	6.7

NOMENCLATURE

C_p = molal heat capacity, B.t.u./lb. mole
E = internal energy, B.t.u./lb. mole
H = enthalpy, B.t.u./lb. mole
P = pressure, lb./sq. inch abs.
T = absolute temperature, °K.
t = temperature, °C.
V = molal volume-cu. ft./lb. mole
J = proportionality factor

ACKNOWLEDGMENT

The authors wish to express their grateful acknowledgment to Oak Ridge National Laboratory and the Union Carbide Nuclear Co., under whose auspices this work was performed.

LITERATURE CITED

(1) Beattie, J. A., Bridgeman, O. C., *Proc. Am. Acad. Arts Sci.* 63, 229 (1928).
(2) Dodge, B. F., "Chemical Engineering Thermodynamics," McGraw-Hill, New York, 1944.
(3) Hoel, P. G., "Introduction to Mathematical Statistics," Wiley, New York, 1947.
(4) Keenan, J. H., Kaye, J., "Gas Tables," Wiley, New York, 1948.
(5) Keenan, J. H., Keyes, F. G., "Thermodynamic Properties of Steam," Wiley, New York, 1936.
(6) Luker, J. A., Gniewek, T., Johnson, C. A., *Ind. Eng. Chem., Chem. Eng. Data Ser.* 3, 3 (1958).
(7) *Ibid.*, p. 8.

Received for review January 16, 1957. Accepted July 23, 1957.

Vapor Pressure and Viscosity of Solutions in the Calcium Oxide-Phosphoric Oxide-Water System at 25°C.

E. O. HUFFMAN, J. D. FLEMING, AND ANTHONY J. SMITH
Division of Chemical Development, Tennessee Valley Authority, Wilson Dam, Ala.

A diversity of interest in the properties of phosphoric acid and calcium phosphate solutions in industrial, agronomic, and biochemical fields has led to the publication of articles concerning various properties of such solutions (*2–4, 6–10, 13, 15*). The vapor pressures and viscosities of solutions in the system calcium oxide–phosphoric oxide–water, as measured by usual methods, are reported here. Compositions of the solutions were bounded by the line phosphoric oxide–water and the solubility isotherms of anhydrous dicalcium phosphate and monocalcium phosphate monohydrate (*2,8*). The solution compositions lay along lines of constant weight ratios of phosphoric oxide–calcium oxide, as shown in Figure 1.

PREPARATION OF SOLUTIONS

The solutions were prepared from conductance water, recrystallized phosphoric acid hemihydrate, and monocalcium phosphate monohydrate. These reagents were prepared by methods described elsewhere (*15*), and their purity was comparable to those of the same reagents used for measurements of density, conductance, and pH (*15*). Stock solutions with the phosphoric oxide–calcium oxide weight ratios shown in Figure 1 were prepared by mixing weighed amounts of monocalcium phosphate monohydrate, water, and phosphoric acid of known concentration. The stock solutions are those represented by the points of highest concentration for each phosphoric oxide–calcium oxide ratio line in Figure 1. For individual measurements, more dilute solutions were prepared by adding water to these stock solutions. The composition of each solution was checked by measuring its density (*15*) and comparing the result with tables of the density-composition relation for solutions in the system (*15*).

METHODS OF MEASUREMENT

Vapor Pressure. The vapor pressure measurements were made by a differential static method. Conductance water was the reference material. As the dimensions of the apparatus were unsuitable for measurement of the vapor pressure of water, a published value, 23.756 mm. of mercury (*14*), was used. The advantages of the differential method for measuring vapor pressures of aqueous salt solutions have been discussed (*12*). The apparatus, Figure 2, was a modification of one described by Gibson and Adams (*12*).

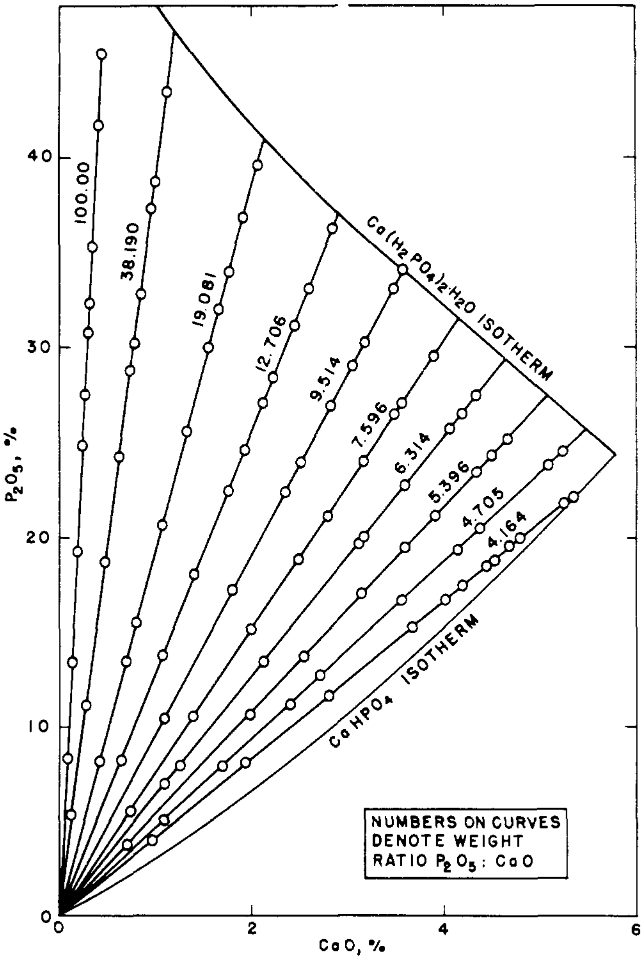

Figure 1. Composition of test solutions