available experimental data of methyl alcohol. For the temperature range $0.9 < T_R < 1.1$, the water density correlation produced densities that permitted the values below $T_R = 0.9$ and above $T_R = 1.1$ to be properly connected with a smooth curve.

The reduced density correlations of ammonia and water were used to develop the isobars above $P_R = 2.5$. The density correlation for ammonia, using Equation 1, applied well in the compressed liquid region and produced values that were within 1.0% of the experimental values. All the isobars up to $P_R = 40$, for temperatures up to $T_R = 1.1$, were developed from the ammonia correlation. However, the ammonia plot was assumed not to apply for reduced temperatures above $T_R = 1.1$, since this correlation failed to produce results that were consistent with available experimental densities, with values resulting from the water-density correlation, and with the Nelson-Obert compressibility charts for pressures below $P_R = 2.5$. On the other hand, the use of the water-density correlation at elevated temperatures produced isobars that properly joined with those obtained at lower temperatures when using the ammonia-density correlation.

CONCLUSIONS

Figures 2 and 3 present the final plots of density for methyl alcohol, which resulted from *P-V-T* data available in the literature and from their extension into regions of pressure and temperature where no data are currently available. Reduced density values read from enlarged plots of Figures 2 and 3 are presented in Table I. The accuracy of the reduced density correlation for methyl alcohol cannot be checked over the complete range of temperature and pressure, but has been checked in regions where data are available, to produce an over-all average deviation of 1.1% resulting from a total of 45 experimental points. The Lydersen, Greenkorn, and Hougen *(13)* density development cannot be properly compared with the results of Figures 2 and 3, since these investigators did not include the behavior of substances with critical compressibility factors below that of water, $z_c = 0.231$.

NOMENCLATURE

P = pressure, atm.
P_c = critical pressure, atm.
P_R = reduced pressure, P/P_c
R = gas constant, 82.055 cm.^{3} atm./gram-mole ° K.
T = absolute temperature, ° K.
T_c = critical temperature, ° K.
T_R = reduced temperature, T/T_c
T_{R_s} = reduced temperature at saturated conditions
v = molar volume, cm.^{3}/gram-mole
v_c = critical molar volume, cm.^{3}/gram-mole
z = compressibility factor, Pv/RT
z_c = critical compressibility factor, $P_c v_c/RT_c$

Greek

μ = dipole moment, debye units
ρ = density, grams/cm.^{3}
ρ_c = critical density, grams/cm.^{3}
ρ_R = reduced density, ρ/ρ_c
ρ_{R_l} = reduced density for saturated liquid
ρ_{R_v} = reduced density for saturated vapor

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RECEIVED for review April 24, 1964. Accepted July 31, 1964.

Standard Heats of Formation of Paraperiodic Acid at 25°

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PERIODIC ACIDS are important compounds representative of the highest oxidation state of iodine, +7. The stable room temperature form in the solid state is paraperiodic acid, H_5IO_6. Its aqueous solution is widely used in iodimetric analytical procedures as an oxidizing agent which is powerful enough to quantitatively oxidize manganous ion to permanganate.

Very little thermodynamic information is available for any forms of periodic acid. Circular 500 of the National Bureau of Standards *(3)* lists some heats of formation based on Thomsen's data *(6)* which are more than 80 years old. Heats of formation of other halogen compounds and ions based on results from the older literature have sometimes been found to be in conflict with more recent values.

Standard heats of formation at 25° of H_5IO_6 (aq.) (−176.5 ± 1.2 kcal./mole) and $H_5IO_6(s)$ (−186.9 ± 1.5 kcal./mole) were determined by combining independently measured heats of reduction in acidic and basic iodide solutions, respectively, with appropriate heats of solution and dilution.

Values of the heat of formation of H_5IO_6 in the solid and infinitely dilute aqueous forms were calculated via two independent sets of directly measured heats of reduction with excess iodide ion in acid and basic solutions respectively.

In acid solution the reduction proceeds according to:

$$H_5IO_6 + 11\,I^- + 7H^+ \rightarrow 4\,I_3^- + 6H_2O$$

while in basic solution:

$$3H_5IO_6 + 3OH^- + I^- \rightarrow 4\,IO_3^- + 9H_2O$$

The stoichiometry of both reactions is well established (*1*). These heats were combined with the pertinent heats of formation of all participants in the reactions and with experimentally measured heats of solution and dilution to obtain the desired standard state values for H_5IO_6.

EXPERIMENTAL

Materials. All chemicals were A. R. grade and their solutions were prepared with distilled water. H_5IO_6 was dried in vacuum at 27° for at least twenty-four hours prior to use. Repeated standard thiosulfate titrations indicated 100.14 ± 0.18% purity within the accuracy of the analytical procedure. The solid periodic acid samples were stored in soft-glass ampoules purged with dry nitrogen prior to sealing.

Calorimeter. The calorimeter has been described elsewhere (*5*), and its over-all accuracy was checked by measurement of the heat of solution of $KCl(s)$ in water. The mean of three determinations corrected to a molar ratio of KCl: 200 H_2O (4.17 ± 0.2 kcal./mole) deviated 0.5% from the average based on the results of eight recent independent studies (*4*) (4.194 ± 0.014 kcal./mole).

All reactions were carried out at 25 ± 0.1° and with 500 ml. of appropriate solution in the dewar. They were initiated by crushing an ampoule containing the periodic acid against the bottom of the dewar. Electrical calibrations were carried out before and after each run to determine the mean energy equivalent of the calorimeter.

RESULTS AND INTERPRETATION

Heats of Reduction. All heats of reduction are given in Tables I and II. Precision indices associated with all average values are standard deviations and concentrations are in moles per liter.

Heats of Dilution. The appropriate heat of dilution correction of the 0.1917*M* H_5IO_6 solution was determined to correct the calorimetric reduction results (Tables I and II) to standard states and all determinations are shown in Table III. Since this heat is unusually high, several other heats of dilution were measured with initial concentrations ranging from 1.193 to 0.02300*M*. Table IV lists all summarized values. No correlation can be made with the thermal behavior of other polybasic acids, since periodic acid with its five replaceable hydrogens is unique. There is a large number of species thought to exist in aqueous solution. These include H_5IO_6, $H_4IO_6^-$, $H_3IO_6^{-2}$, $H_2IO_6^{-3}$, HIO_6^{-4}, IO_4^-, and $I_2O_9^{-4}$ (*2*). It is likely that the large heats of dilution are related to the undoubtedly complex equilibria between these and perhaps other species. It may be noted from the data in Table IV that the heats of dilution decrease regularly with a sharp decline beginning in the region below 0.1*M* H_5IO_6.

Heats of Solution. Heats of solution of $H_5IO_6(s)$ were measured to very low final concentrations and are shown in Table V. Variations in the amount of solid sample per run and consequently in final concentrations (0.008–0.002*M*) gave essentially constant heats.

Standard Heats of Formation of H_5IO_6(aq.) and $H_5IO_6(s)$. The standard heats of formation were calculated using the recent data of Wu, Birky, and Hepler (*7*) for triiodide and iodate ions. All other pertinent auxiliary data were taken from Circular 500 (*3*).

Table I. Heat of Reduction of 0.1917*M* H_5IO_6 with Iodide Ion in Acid Solution

Millimoles 0.1917*M* H_5IO_6 in Ampoule	Millimoles 0.30*M* NaI	Millimoles 0.60*M* $HClO_4$	− Total Energy Change, Cal.	$-\Delta H_1$, Kcal./Mole H_5IO_6
5.453	150	300	70.4	129.1
5.569	150	300	71.8	129.0
5.592	150	300	71.9	128.7
5.689	150	300	73.1	128.4

Av. $\Delta H_1 = -128.8 \pm 0.3$ kcal./mole H_5IO_6.

Table II. Heat of Reduction of 0.1917*M* H_5IO_6 with Iodide Ion in Basic Solution

Millimoles 0.1917*M* H_5IO_6 in Ampoule	Millimoles 0.05*M* NaI	Millimoles 0.20*M* NaOH	− Total Energy Change, Cal.	$-\Delta H_2$, Kcal./Mole H_5IO_6
1.923	25	100	64.8	33.6
1.971	25	100	65.2	33.1
1.973	25	100	63.0	32.0
2.016	25	100	63.0	31.2
2.122	25	100	68.5	32.3
2.137	25	100	69.2	32.4

Av. $\Delta H_2 = -32.4 \pm 0.8$ kcal./mole H_5IO_6.

Table III. Heat of Dilution of 0.1917*M* H_5IO_6

Millimoles 0.1917*M* H_5IO_6 in Ampoule	Moles H_2O	Total Energy Change, Cal.	ΔH_3, Kcal./Mole H_5IO_6
1.525	27.5	11.5	7.52
1.513	27.5	11.2	7.41
1.417	27.5	10.8	7.59
1.520	27.5	11.4	7.50
1.237	27.5	9.08	7.34

Av. $\Delta H_3 = 7.47 \pm 0.10$ kcal./mole H_5IO_6.

Table IV. Additional Heats of Dilution of H_5IO_6 Solutions

$M_{H_5IO_6}$ in Ampoule[a]	Av. ΔH_D, Kcal./Mole H_5IO_6	Number of Determinations
1.193	10.2 ± 0.2	3
0.7056	9.48 ± 0.06	3
0.3532	8.54 ± 0.16	3
0.1917	7.47 ± 0.10	5
0.09586	6.60 ± 0.18	3

[a] Final concentrations in all cases ranged from 0.0021*M* to 0.0028*M*.

Table V. Heat of Solution of $H_5IO_6(s)$

Millimoles H_5IO_6 in Ampoule	Moles H_2O	Total Energy Change	ΔH_s, Kcal./Mole
3.988	27.5	42.9 cal.	10.8
3.522	27.5	38.5	10.9
3.835	27.5	36.1	9.41
3.083	27.5	34.6	11.2
2.256	27.5	22.6	10.0
1.867	27.5	18.8	10.0
2.095	27.5	20.6	9.85
1.149	27.5	12.6	10.9
1.282	27.5	12.4	9.95
1.212	27.5	13.0	10.8

Av. $\Delta H_s = 10.4 \pm 0.6$ kcal./mole $H_5IO_6(s)$.

Combining the average ΔH_1 (-128.8 ± 0.3 kcal./mole) from Table I with appropriate heats of formation and dilution corrections from Table III, gives ΔH_f° of H_5IO_6(aq.) = -175.9 kcal./mole.

Similarly, the average ΔH_2 (-32.4 ± 0.8 kcal./mole) from Table II yields $\Delta H_f^\circ = -177.2$ kcal./mole for H_5IO_6(aq.). The agreement between these two independently determined values is good and their mean gives ΔH_f° of H_5IO_6(aq.) = -176.5 kcal./mole with an estimated over-all uncertainty of ± 1.2 kcal./mole. ΔH_f° of $H_5IO_6(s)$ is -186.9 ± 1.5 kcal./mole and was obtained by combining ΔH_f° of H_5IO_6(aq.) with the average heat of solution from Table V.

Circular 500 (*3*) lists the heats of formation of H_5IO_6(aq.) and $H_5IO_6(s)$ as -183.0 and -184.4 kcal./mole, respectively. These values are based on Thomsen's heats of reduction of $0.23M$ H_5IO_6 with $SnCl_4^{-2}$ in acid solution (*6*). Since no heats of dilution were reported we believe that our values are more reliable.

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Received for review April 28, 1964. Accepted June 29, 1964.

Volumetric and Latent Heat of Vaporization Measurements for *trans*-2-Butene

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The specific volumes of the liquid and dense phases of *trans*-2-butene were measured at pressures up to 5000 p.s.i. in the temperature interval between 40° and 400° F. The latent heat of vaporization was determined from calorimetric measurements at temperatures between 100° and 250° F. The results are presented in graphical and tabular form together with comparisons with earlier published data.

THE THERMODYNAMIC properties of *trans*-2-butene have not been studied in great detail. Lamb and Roper (*8*) measured the vapor pressure of this compound at temperatures between −91° and 49° F., while Kistiakowsky (*7*) reported values at temperatures from −108° to 76° F. Guttman and Pitzer (*4*) measured the vapor pressure of *trans*-2-butene at temperatures between −96° and 34° F. and also determined the latent heat of vaporization of this compound at a temperature in the vicinity of 34° F. The specific weight of the bubble-point liquid has been reported (*1*). The available experimental information did not seem sufficient to establish with certainty the volumetric behavior in the liquid phase nor the latent heat of vaporization of this compound. For this reason, measurements were made of the volumetric behavior of the liquid phase at pressures up to 5000 p.s.i. in the temperature interval between 40° and 400° F. and of the latent heat of vaporization at temperatures between 100° and 250° F.

MATERIALS

The *trans*-2-butene employed for both the volumetric and calorimetric measurements was obtained from the Phillips Petroleum Co. and was reported to contain less than 0.2 mole % of impurity. After appropriate deaeration, the sample showed from a special set of measurements less than 0.25 p.s.i. variation in vapor pressure with change in quality from 0.1 to 0.9 at 160° F. This set of measurements was not employed in evaluating the actual vapor pressure of *trans*-2-butene reported here.

VOLUMETRIC MEASUREMENTS

Utilizing available pressure-volume-temperature equipment, the volumetric behavior of *trans*-2-butene in the liquid phase was established. In principle, the apparatus involved a stainless steel pressure vessel within which a sample of known weight was confined over mercury. The