($[S]_0 - [S]_t$) *vs.* t_0' was constructed and from this plot, which was linear within the limits of experimental error, a value of $v_0 = 12.2 \times 10^{-6}$ *M*/min. was obtained.

In addition to the application described above the nomogram developed in this communication has proved to be useful in predicting the effect of changes in values of K_S, K_P and K_I and of $[S]_0$ and $[I]$ upon the initial velocities and thus has provided a rapid and convenient way to anticipate the consequences of a particular experiment and whether such an experiment will be definitive.

The authors wish to express their indebtedness to Mr. Charles Goebel for his assistance in the construction of the nomogram described in this communication.

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GATES AND CRELLIN LABORATORIES OF CHEMISTRY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA 4, CALIFORNIA

The Vapor Pressure of Bromine from 24 to 116°[1]

BY JACK FISCHER AND JAMES BINGLE

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The vapor pressure of bromine was determined from 24 to 116° in a nickel and Monel apparatus in which the vapor was cycled through the liquid with the use of a magnetically operated pump.

The apparatus employed in this investigation has been described in another publication.[2] Reagent grade bromine was purified by distilling off a large portion, about one-quarter of the original volume, at room temperature, to remove any chlorine present. The remainder was passed over phosphorus pentoxide in order to remove traces of water before adding it to the system. The sample to be used was condensed in a fluorothene trap cooled with liquid nitrogen. Approximately 15- to 20-ml. portions were collected in the trap at a time. Each portion was frozen, evacuated and thawed several times to remove non-condensable gases. A 3- to 4-ml. portion of the bromine in the trap was distilled off to remove any further impurities more volatile than bromine. The residual amount of bromine was then distilled into the equilibrium cell of the apparatus. The process was repeated until 80–90 ml. of bromine had been collected in the equilibrium cell.

Vapor pressure measurements were made when a constant value for the vapor pressure at 75° was obtained after removing successive fractions of bromine from the system. The fact that the reduction of the volume of bromine to half its value produced no change in vapor pressure at 75° is evidence of its purity.

The vapor pressure of bromine from 24 to 116° is expressed by the equation

$$\log p = -\frac{2199.0}{T} - 4.150 \log T + 19.9618 \quad (1)$$

where p = pressure in millimeters, T = temperature °K. The data are shown in Table I and the log of the pressure in millimeters is plotted against the temperature in Fig. 1. The pressures obtained by Ramsay and Young[3] and those obtained by Scheffer and Voogd[4] are plotted in Fig. 2 together with our values over a representative range. Our values agree with those of Ramsay and Young within experimental error and are only slightly lower than those of Scheffer and Voogd. We have probably achieved a better removal of more volatile impurities. Values for the vapor

TABLE I

VAPOR PRESSURE OF BROMINE, 24 TO 116°

Temp., °C.	Observed pressure mm.	% dev. Obsn. *vs.* calcn. eq. 1	Temp., °C.	Observed pressure mm.	% dev. Obsn. *vs.* calcn. eq. 1
24.48	202	−0.5	70.16	1083	+0.3
26.66	223	.0	74.87	1246	− .1
32.37	283	.0	79.80	1439	− .1
43.44	437	+ .2	85.89	1716	+ .2
49.67	548	+ .2	93.91	2129	+ .2
55.00	662	+ .5	100.86	2527	− .5
60.32	787	− .3	107.04	2957	.0
64.06	892	+ .1	111.21	3268	+ .1
66.90	977	+ .1	116.19	3662	− .1
				Av.	±0.19

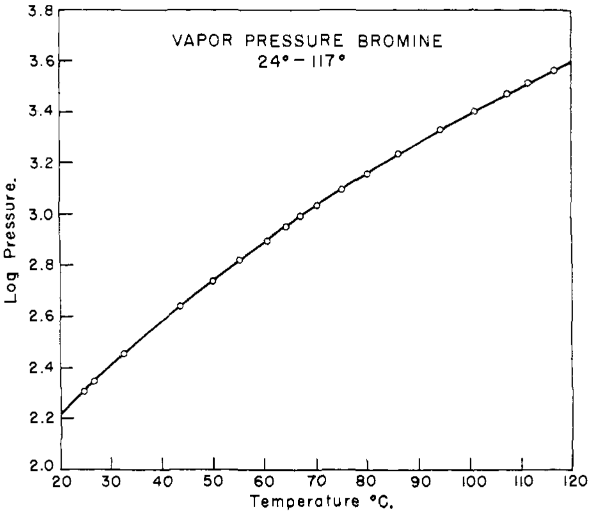

Fig. 1.—$\text{Log}_{10}\ p$ (in mm.) *vs.* temperature, °C.

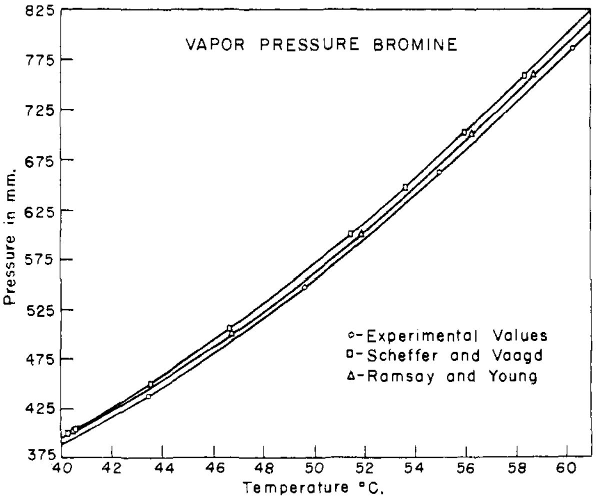

Fig. 2.—Vapor pressure (mm.) of bromine *vs.* temperature, °C.

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. Fischer, J. Bingle and R. C. Vogel, THIS JOURNAL, in press.

[3] J. Ramsay and J. Young, *J. Chem. Soc.*, **49**, 453 (1886).

[4] F. E. C. Scheffer and M. Voogd, *Rec. trav. chim.*, **45**, 214 (1920).

pressure of bromine trifluoride and bromine pentafluoride at 75 and 100° using this apparatus agree very well with the literature values obtained with a nickel and Monel ebulliometer. This comparison at 75° is as follows:

	Our values, mm.	Lit. values, mm.
BrF_3	111	110.91[5]
BrF_5	2247	2249.2[5]

A similar comparison at 100° is

BrF_3	309	308.87[5]

The experimental values for the vapor pressure of bromine shown in Table I agree with values calculated from eq. 1, with an average deviation of ±0.2%. The temperatures were measured to ±0.01° and may be assumed to be accurate to ±0.02°. The pressure measurements are accurate to ±0.5 mm.

(5) R. D. Long, Argonne National Laboratory Document ANL-5405.

CHEMICAL ENGINEERING DIVISION
ARGONNE NATIONAL LABORATORY
LEMONT, ILLINOIS

Heats of Formation of Niobium Carbide and Zirconium Carbide from Combustion Calorimetry

BY ALLA D. MAH AND B. J. BOYLE

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Refractory metal carbides, although of constantly increasing technical importance, are difficult to prepare in a form adequately pure for thermodynamic measurements. As a consequence, the available thermodynamic data are scattered and incomplete. This note presents the results of combustion calorimetric investigations of two substances, niobium carbide (columbium carbide) (NbC) and zirconium carbide (ZrC). Although the purity of the substances available for study leaves much to be desired, it is believed that useful heat of formation data have been obtained. The literature contains no previous directly measured values for these substances.

Materials and Methods.—The niobium and zirconium carbides were prepared by Professor Leo Brewer and coworkers of the Chemistry Department of the University of California.

Niobium carbide was prepared from niobium metal (containing no impurities other than trace amounts of silver, calcium, copper, iron, silicon and tantalum) and Acheson graphite. These substances were mixed and heated *in vacuo* in a graphite container to 2300–2400°. The product appeared uniform upon microscopic examination and X-ray diffraction showed the presence of only the niobium carbide phase. Analysis gave 10.82% carbon and 89.10% niobium (corresponding to $NbC_{0.939}$), as compared with the theoretical 11.45 and 88.55%. The unaccounted for 0.08% was considered to be oxygen and nitrogen.

Zirconium carbide was prepared similarly from Acheson graphite and part of the same sample of hafnium-free zirconium sponge used by Humphrey[1] in his heat of formation determinations of zirconium dioxide. In this case also a uniform appearing product, showing only the zirconium carbide phase upon X-ray examination, was obtained. Analysis gave 11.07% carbon and 88.15% zirconium, as compared with the theoretical 11.63 and 88.37%. The unaccounted for 0.78% could be attributed only to nitrogen and oxygen picked up during the course of preparation.

The energy of combustion determinations were made with previously described apparatus.[2] All weights were corrected to vacuum and all heat values are in terms of the defined calorie (1 cal. = 4.1840 abs. joules). National Bureau of Standards benzoic acid sample No. 39g was used for calibration. Two bombs were employed and the calibration values were 32,480.6 (±0.02%) cal./ohm for the niobium carbide combustions and 32,426.2 (±0.02%) cal./ohm for the zirconium carbide combustions.

All combustions were made under 30 atm. oxygen pressure, with no water added to the bomb. Ignition of the samples was by means of an electrically heated platinum spiral and a filter paper fuse. The bomb gases, after combustion, were tested for carbon monoxide, which was found to be negligible (less than 0.00003%). The bomb gases also were analyzed for oxides of nitrogen for which a small energy correction, ranging from 0.001 to 0.002%, was required.

The niobium carbide was held in the bomb on a niobium pentoxide plate, supported in turn by an alundum disc. About 91% of the niobium pentoxide from the combustion appeared as a fused layer upon the niobium pentoxide plate and the remainder appeared as a fine wall deposit on the bomb. X-Ray diffractions of the original niobium pentoxide plate and the adhering layer of niobium pentoxide from the combustion showed them to be the high temperature variety reported by Brauer.[3] The wall deposit was a mixture of this variety and another, similar to Humphrey's[1] findings in his niobium metal combustions. The combustion products were examined visually for evidence of incomplete combustion, and three runs in which blackish specks were observed were discarded.

The zirconium carbide was held in silica glass capsules heavily lined with monoclinic zirconium dioxide. Over 99.9% of the zirconium dioxide formed by combustion remained in the capsule and less than 0.1% appeared as a wall deposit on the bomb. X-Ray diffraction of both fractions showed only monoclinic zirconium dioxide. Comparison of the mass of the combustion product with the original mass of the carbide (taking into account its analysis) indicated that the combustions were complete.

Energy of Combustion Results.—The results of the measurements are given in Table I. In both instances the precision uncertainty is about 0.03%.

Two assumptions were made regarding the composition of the niobium carbide sample to permit calculation of the correction to be made for impurities; both are consistent with the chemical analysis. First, the sample was considered as composed of 99.39% of the carbide phase, $NbC_{0.945}$, and 0.61% niobium nitride (NbN). This assumption leads to a correction of 6.8 cal./g. Second, it was assumed that the sample is 99.46% carbide of composition $NbC_{0.944}$ and 0.54% oxide (as NbO). This leads to a correction of 8.0 cal./g. The mean value 7.4 cal./g. has been applied in Table I. In obtaining these values the heats of solid solution of the nitride and oxide in the carbide phase are assumed to be zero.

Two similar assumptions were made for correcting the zirconium carbide results. First, the sample was assumed to be 94.01% zirconium carbide (ZrC), 5.86% zirconium nitride (ZrN) and 0.13% free carbon. This leads to 72.7 cal./g. correction. Second, it was assumed that the sample contains 94.72% zirconium carbide (ZrC), 5.23% zirconium oxide (as ZrO) and 0.05% free carbon, which leads to 92.0 cal./g. correction. Again, the heats of solid solution of the nitride and oxide in the carbide phase are taken as zero. In the absence of a decisive criterion for choice between these corrections, it was considered best to apply the mean value, 82.4 cal./g., in Table I.

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[1] G. L. Humphrey, THIS JOURNAL, **76**, 978 (1954).

[2] G. L. Humphrey, *ibid.*, **73**, 1587 (1951).

[3] G. Brauer, *Z. anorg. Chem.*, **248**, 1 (1941).