indispensable when it is necessary to determine accurately the depth of a very shallow layer.

Manuscript received Sept. 25, 1961. This work was supported in part by the Air Force Cambridge Research Laboratory AF 19(604)8060.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1962 JOURNAL.

REFERENCES

1. W. W. Happ and W. Shockley, *Bull. Am. Phys. Soc.*, Ser. II **1**, 382 (1956).
2. C. S. Fuller and J. A. Ditzenberger, *J. Appl. Phys.*, **27**, 544 (1956).
3. B. Jansen, *Solid State Electronics*, **2** [1], 14 (1961).
4. B. McDonald and F. C. Collins, *Bull Am. Phys. Soc.*, Ser. II **6**, 106, (1961).
5. E. Tannenbaum, *Solid-State Electronics*, **2** [2/3], 123, March (1961).

Vapor Pressure of Gallium, Stability of Gallium Suboxide Vapor, and Equilibria of Some Reactions Producing Gallium Suboxide Vapor

C. N. Cochran and L. M. Foster

Alcoa Research Laboratories, Physical Chemistry Division, Aluminum Company of America,
New Kensington, Pennsylvania

ABSTRACT

Vapor pressures of gallium in the literature are too high because $Ga_2O(v)$ formed in the reaction of gallium with the quartz effusion cells used for the measurements. Gallium was found to be less reactive with alumina than with quartz. Measurements in an alumina effusion cell gave vapor pressures for gallium that obey the expression

$$\log P\ (\text{atm}) = -14{,}900/T - 0.515 \log T + 7.34$$

Values for $\Delta H_{f\,298[Ga_2O\,(v)]}$ of -17.4 ± 0.7 and -19.7 ± 0.7 kcal/mole were found for the reaction of gallium with quartz and magnesium oxide, respectively. The latter value was employed to calculate the equilibria in forming $Ga_2O(v)$ from the following pairs of reactants: gallium-gallia, graphite-gallia, tin-gallia, gallium-alumina, and gallium-water vapor. The vapor pressures of silver and tin were determined and compared with literature values to check the constants of the system.

Previous measurements (1, 2) of the vapor pressure of gallium employed the Knudsen method with quartz effusion cells. However, a mass spectroscopic study of Antkiw and Dibeler (3) showed that considerable concentrations of $Ga_2O_{(v)}$ formed from reaction of gallium with a quartz crucible at 865°-1025°C. This indicates that the reported vapor pressure data for gallium are too high.

In the present work an alumina effusion cell was used to measure the vapor pressure of gallium. Additions of quartz or magnesium oxide were made to the gallium in the cell to form gallium suboxide. The differences in the effusion rates with and without quartz or magnesium oxide are used to derive the heat of formation of gallium suboxide vapor.

Experimental

A single sintered alumina (99+% pure) effusion cell, 15 mm ID, 30 mm deep, with an orifice 0.90 mm in diameter and 0.37 mm thick, was employed in obtaining all of the data. Reactions between the charge materials and the alumina cell were negligible. The weight loss of the cell in an effusion experiment was always considerably less than 1% of the total weight loss. A cell constant of 0.00098 and a Clausing factor of 0.71 were calculated for the orifice.

In two experiments where silver was employed in the cell, the orifice was covered with a tight fitting cover of sintered alumina. By comparing the loss in this case with that when the orifice was uncovered, 46 ± 5% of the total loss with the orifice uncovered was found to occur through the lapped seal between the removable cover and the body of the cell. With this "leakage" taken into account, the following relationship between pressure and effusion losses from the cell was obtained

$$\text{Pressure}_{(\text{atm})} = \frac{0.00075\ (\text{effusion rate in g/hr})\, T^{1/2}}{(\text{molecular weight vapor})^{1/2}}$$

The rates of weight loss were determined with an automatic, recording, vacuum analytical balance, modeled after the microbalance described elsewhere (4). Only data from the linear portions of the weight loss-time plots were used. This practice eliminated errors in effusion rate determination caused by outgassing of the cell and its contents as steady-state conditions were approached. Usually, steady-state conditions were reached within ½ hr after reaching temperature.

Temperatures were regulated to within ±1°C by a Foxboro Recorder-Controller, Model 8253-201R, with the control thermocouple located between windings of the furnace element at a position corresponding to the midpoint of the cell. The relationship between the temperature of the control couple and the

Table I. Gallium vapor pressure data
$Ga_{(l)} \rightleftharpoons Ga_{(v)}$

	No quartz present								Quartz added	
°K	Effusion rate, mg/hr	Gallium vapor pressure, atm	$-\Delta\frac{F^\circ_T - H^\circ_{298}}{T}$	$\frac{\Delta F^\circ_T}{T}$	$\frac{\Delta H^\circ_{298}}{T}$	ΔH°_{298}	$\frac{68,960}{T}$	$P_{calc.}$, atm	Effusion rate, mg/hr	Apparent gallium vapor pressure, atm*
1179	0.050	1.53×10^{-7}	27.03	31.17	58.20	68,620	58.49	1.3×10^{-7}	0.126	3.9×10^{-7}
1231	0.15	4.69×10^{-7}	26.96	28.94	55.90	68,810	56.02	4.4×10^{-7}	0.39	1.2×10^{-6}
1280	0.38	1.21×10^{-6}	26.90	27.06	53.96	69,070	53.88	1.3×10^{-6}	1.21	3.9×10^{-6}
1332	1.07	3.47×10^{-6}	26.84	24.97	51.81	69,010	51.77	3.5×10^{-6}	3.7	1.2×10^{-5}
1357	1.56	5.11×10^{-6}	26.81	24.20	51.01	69,220	50.82	5.6×10^{-6}	6.7	2.2×10^{-5}
1383	2.64	8.75×10^{-6}	26.78	23.14	49.92	69,040	49.86	9.0×10^{-6}	11.6	3.8×10^{-5}
						Avg. 68,960 ± 190				
2300			26.00				29.99	0.134		
2400			25.94				28.74	0.244		
2500			25.88				27.59	0.421		
2676			25.77				25.77	1.00		

* Effusion of $Ga_2O_{(v)}$ and $Ga_{(v)}$ from cell treated as being entirely $Ga_{(v)}$.

cell was determined with a second thermocouple in a separate experiment.

Materials

Alcoa GA-6 grade, 99.9999+% pure gallium, Tadanac Brand (Consolidated Mining and Smelting Company of Canada, Ltd., Trail, B. C.) 99.9999% silver, and Fisher Scientific Company's 99.97% tin were employed in this work. In the Ga-SiO_2 and Ga-MgO experiments, the gallium was covered with a bed of 4 to 8-mesh chips of ordinary fused quartz, and pellets (⅛ in. in diameter and ⅛-¼ in. long) of Fisher Scientific Company's 99.93% magnesium oxide, respectively.

Vapor Pressure of Gallium

Vapor pressures calculated from the effusion data for gallium are given in Table I and compared with literature values in Fig. 1. The values from the present work range from fourfold lower at 1100°C to fivefold lower at 900°C than the values selected by Stull and Sinke (5) from previously published data.

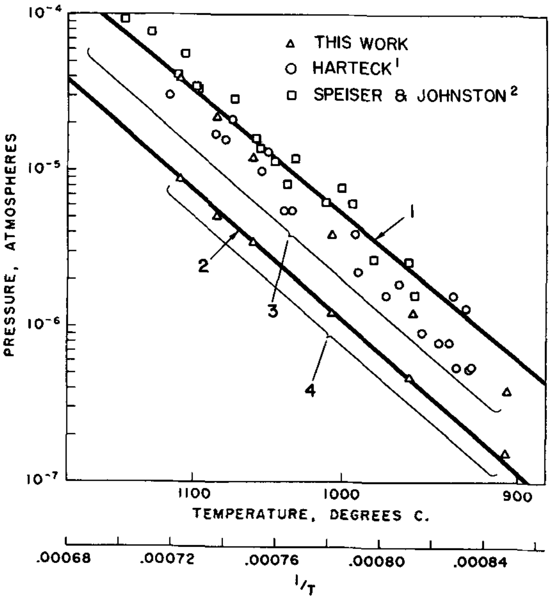

Fig. 1. Gallium vapor pressure data. 1, Third law extrapolation of previous data by Stull and Sinke (5), $\Delta H^\circ_{v\,298} = 65.00$ kcal/mole; 2, third law extrapolation of data from this work, $\Delta H^\circ_{v\,298} = 68.96$ kcal/mole; 3, measured in presence of quartz; 4, measured in an alumina effusion cell.

With the vapor considered as being monatomic, as indicated in mass spectroscopic studies (3,6), $\log P = -14{,}900/T - 0.515 \log T + 7.34$, $\Delta H^\circ_{v\,298} = 68.96 \pm 0.19$ kcal, and the boiling point is 2676°K. Stull and Sinke (5) chose $\Delta H^\circ_{v298} = 65.00$ kcal and a boiling point of 2510°K.

Drowart and Honig (6) found the heat of vaporization of gallium from beryllia and graphite crucibles to be 59 ± 4 kcal/mole by second law treatment of ion intensities in a mass spectroscopic study. It is recognized that their procedure might give only approximate results.

Apparent monatomic gallium pressures were calculated from the gallium-quartz effusion data and also plotted in Fig. 1. These data were found to fall within the band of pressures reported by the previous workers who vaporized gallium from quartz. These values show the same systematic deviation from the third law extrapolation line of Stull and Sinke (5) as do the data of the previous workers. This deviation is another proof, as noted by Drowart and Honig (6), that these data cannot be represented simply by vaporization of monatomic gallium.

Stability of Ga_2O Vapor

Before information on the stability of $Ga_2O_{(v)}$ could be obtained from the effusion data with quartz or magnesium oxide added to the gallium, the most favorable of the possible reactions had to be determined. This was accomplished in each case by finding the reaction that resulted in the least negative value of $\Delta H^\circ_{f\,298[Ga_2O_{(v)}]}$ and that showed no systematic deviation of this quantity with temperature. Using these criteria, the steady-state reaction between quartz and gallium is

$$2Ga_{(l)} + SiO_{2(c)} \rightleftharpoons SiO_{(v)} + Ga_2O_{(v)} \qquad [1]$$

However, calculations showed that the initial reaction of quartz with gallium produces silicon (reaction [2])

$$4Ga_{(l)} + SiO_{2(c)} \rightleftharpoons Si_{(in\ Ga)} + 2Ga_2O_{(v)} \qquad [2]$$

This dissolves in the gallium until its activity is large enough that any further silicon produced will react with the quartz to produce $SiO_{(v)}$ (reaction [3]) and give the same over-all reaction as [1].

Table II. Calculation of ΔH°_{298} for the reactions and $\Delta H^\circ_{f\,298}$ for $Ga_2O_{(v)}$

$2Ga_{(l)} + SiO_{2(c)} \rightleftarrows SiO_{(v)} + Ga_2O_{(v)}$

°K	Total effusion rate, mg/hr	Correction for Ga evaporation, mg/hr	Ga_2O loss, mg/hr	SiO loss, mg/hr	P_{Ga_2O}, atm	P_{SiO}, atm	K	$\frac{\Delta F^\circ_T}{T}$	$-\Delta\left[\frac{F^\circ_T - H^\circ_{298}}{T}\right]$	$\frac{\Delta H^\circ_{298}}{T}$	ΔH°_{298}
1179	0.126	0.043	0.065	0.018	1.3×10^{-7}	6.9×10^{-8}	9.0×10^{-15}	64.25	79.63	143.88	169,630
1231	0.39	0.14	0.195	0.055	4.1×10^{-7}	2.2×10^{-7}	9.0×10^{-14}	59.67	79.31	138.98	171,080
1280	1.21	0.40	0.63	0.18	1.3×10^{-6}	7.2×10^{-7}	9.4×10^{-13}	55.01	79.02	134.03	171,560
1332	3.7	1.1	2.0	0.57	4.4×10^{-6}	2.3×10^{-6}	1.0×10^{-11}	50.31	78.71	129.02	171,860
1357	6.7	1.7	3.9	1.1	8.6×10^{-6}	4.5×10^{-6}	3.9×10^{-11}	47.61	78.56	126.17	171,210
1383	11.6	2.7	6.9	2.0	1.5×10^{-5}	8.2×10^{-6}	1.2×10^{-10}	45.37	78.41	123.78	171,190

Avg. $\Delta H^\circ_{298} = 171{,}070 \pm 690$

At 298°K, $\Delta H^\circ_{f\,Ga_2O} = \Delta H^\circ_{reaction} + \Delta H^\circ_{f\,SiO_{2(c)}} - \Delta H^\circ_{f\,SiO_{(v)}} = 171{,}070 - 209{,}900 + 21{,}411 = -17{,}420 \pm 690$ cal/mole

$2Ga_{(l)} + MgO_{(c)} \rightleftarrows Mg_{(v)} + Ga_2O_{(v)}$

°K	Total effusion rate, mg/hr	Correction for Ga evaporation, mg/hr	Ga_2O loss, mg/hr	Mg loss, mg/hr	P_{Ga_2O}, atm	P_{Mg}, atm	K	$\frac{\Delta F^\circ_T}{T}$	$-\Delta\left[\frac{F^\circ_T - H^\circ_{298}}{T}\right]$	$\frac{\Delta H^\circ_{298}}{T}$	ΔH°_{298}
1179	0.100	0.043	0.049	0.0077	1.0×10^{-7}	4.0×10^{-8}	4.0×10^{-15}	65.86	68.60	134.46	158,530
1231	0.85	0.14	0.18	0.028	3.8×10^{-7}	1.5×10^{-7}	5.7×10^{-14}	60.58	68.31	128.89	158,660
1280	0.89	0.40	0.42	0.066	9.0×10^{-7}	3.6×10^{-7}	3.2×10^{-13}	57.15	68.05	125.20	160,260
1332	2.9	1.1	1.6	0.25	3.5×10^{-6}	1.4×10^{-6}	4.9×10^{-12}	51.78	67.78	119.51	159,190
1383	7.2	2.7	3.9	0.62	8.7×10^{-6}	3.5×10^{-6}	3.0×10^{-11}	48.13	67.51	115.64	159,930

Avg. $\Delta H^\circ_{298} = 159{,}310 \pm 680$

At 298°K, $\Delta H^\circ_{f\,Ga_2O} = \Delta H^\circ_{reaction} + \Delta H^\circ_{f\,MgO_{(c)}} - \Delta H^\circ_{f\,Mg_{(v)}} = 159{,}310 - 143{,}700 - 35{,}330 = -19{,}720 \pm 680$ cal/mole

$$Si_{(in\ Ga)} + SiO_{2(c)} \rightleftarrows 2SiO_{(v)} \qquad [3]$$

Similar calculations show that the steady-state reaction of gallium with magnesium oxide is

$$2Ga_{(l)} + MgO_{(c)} \rightleftarrows Mg_{(v)} + Ga_2O_{(v)} \qquad [4]$$

Gallium saturates rapidly with magnesium from the reaction to achieve a steady-state condition.

The effusion data from experiments where quartz and magnesium oxide were added are listed in Table II. After correcting the effusion losses for metal vaporization, the remaining weight losses were divided stoichiometrically between the gaseous products according to the reaction equations. Partial pressures and equilibrium constants were calculated and converted to free energy changes. These in turn were converted to values of ΔH°_{298} with the aid of free energy function data discussed in a later section. Values of ΔH°_{298} were used together with values of $\Delta H^\circ_{f\,298}$ for the other reactants and products to calculate values of —17.4 ± 0.7 and —19.7 ± 0.7 kcal/mole for $\Delta H^\circ_{f\,298[Ga_2O_{(v)}]}$ from the quartz and magnesium oxide reactions, respectively.

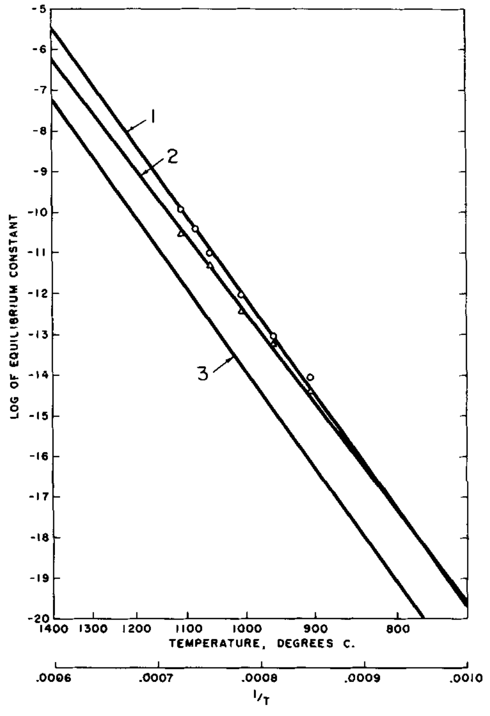

Fig. 2. Equilibrium constants for reaction of gallium with quartz and with magnesium.

1. $2Ga_{(l)} + SiO_{2(c)} \rightleftarrows SiO_{(v)} + Ga_2O_{(v)}$, $\Delta H^\circ_{298} = 171.1$ kcal
2. $2Ga_{(l)} + MgO_{(c)} \rightleftarrows Mg_{(v)} + Ga_2O_{(v)}$, $\Delta H^\circ_{298} = 159.3$ kcal
3. $4Ga_{(l)} + SiO_{2(c)} \rightleftarrows Si_{(c)} + 2Ga_2O_{(v)}$, $\Delta H^\circ_{298} = 175.1$ kcal

Other workers have found evidence recently that the presently accepted heat of formation for silica used in this work may be too positive. Taylor (7) and co-workers believe that the error in this value may be about 4.5 kcal/mole. A tentative calculation by Good (8) places the error at between 6-8 kcal/mole. If all of the difference in the values of $\Delta H^\circ_{f\,298[Ga_2O_{(v)}]}$ obtained from the quartz and magnesium oxide experiments in this work is assigned to an error in $\Delta H^\circ_{f\,298[SiO_2]}$, the error becomes 2 x 2.3 = 4.6 kcal/mole. (The difference of 2.3 kcal is multiplied by two because the heat of formation of SiO that is employed will become 2.3 kcal more negative at the same time.) The value of $\Delta H^\circ_{f\,298[Ga_2O_{(v)}]}$ calculated from the gallium-magnesium oxide experiments will be employed in all further calculations because of the good agreement between the 4.6 kcal/mole error in the value of $\Delta H^\circ_{f\,298[SiO_{2(c)}]}$ that we calculated using it and the 4.5 kcal/mole that Taylor and co-workers calculated.

The fit of all of the effusion data to the third law extrapolation of these data is shown in Fig. 2. The equilibrium constants for reaction [2], are also shown in Fig. 2. These equilibrium constants are the

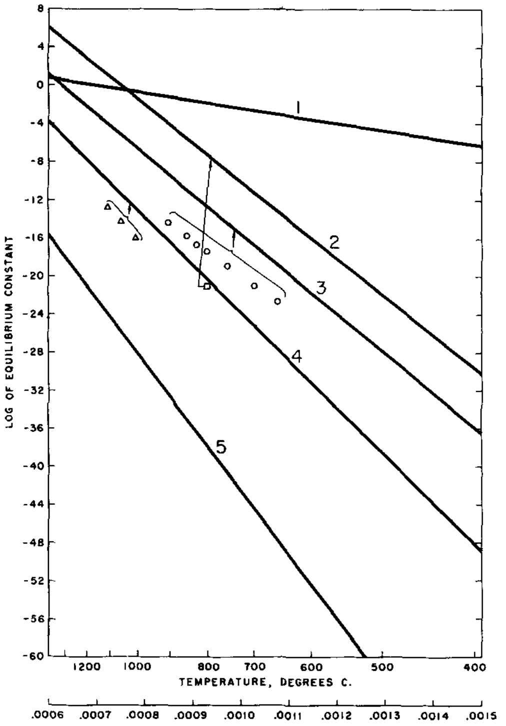

Fig. 3. Equilibrium constants of some reactions forming gallium suboxide based on $\Delta H^\circ_{f\ 298[Ga_2O_{(v)}]} = -19.7$ kcal

1. $H_2O_{(v)} + 2Ga_{(l)} \rightleftharpoons Ga_2O_{(v)} + H_2O_{(v)}$, $\Delta H^\circ_{298} = 38.1$ kcal
2. $2C_{(c)} + Ga_2O_{3(c)} \rightleftharpoons Ga_2O_{(v)} + 2CO_{(v)}$, $\Delta H^\circ_{298} = 185.5$ kcal
3. $4Ga_{(l)} + Ga_2O_{3(c)} \rightleftharpoons 3Ga_2O_{(v)}$, $\Delta H^\circ_{298} = 198.9$ kcal
4. $2Sn_{(l)} + Ga_2O_{3(c)} \rightleftharpoons 2SnO_{(v)} + Ga_2O_{(v)}$, $\Delta H^\circ_{298} = 236.3$ kcal
5. $4Ga_{(l)} + Al_2O_{3(c)} \rightleftharpoons Al_2O_{(v)} + 2Ga_2O_{(v)}$, $\Delta H^\circ_{298} = 321.6$ kcal

Points represent apparent equilibrium constants calculated from Knudsen effusion experiments *in which equilibrium was not attained.*

same whether they are calculated from the uncorrected heat of formation of quartz and the heat of formation of gallium suboxide from the gallium-quartz experiments or from the corrected value for quartz and the value for gallium suboxide from the gallium -magnesium oxide experiments.

Equilibria of Some Other Reactions Producing $Ga_2O_{(v)}$

Calculated equilibrium constants are shown in Fig. 3 for a number of other reactions that produce $Ga_2O_{(v)}$. The small equilibrium constants calculated for the reaction of gallium with alumina are substantiated by the low reactivity between gallium and alumina found in this work. The equilibria of the reaction of gallium with water vapor will be employed along with the equilibria of the quartz-gallium reactions in the following paper dealing with implications of these reactions in the synthesis of gallium arsenide in quartz systems.

The reactions of tin, graphite, and gallium with gallia, shown in Fig. 3, were employed in other attempts to measure the stability of $Ga_2O_{(v)}$. However, equilibrium was not achieved in these cases. The apparent equilibrium constants that were obtained from the effusion rates were always less than the corresponding equilibrium constants calculated with the $\Delta H^\circ_{f\ 298[Ga_2O_{(v)}]}$ from the magnesium oxide-gallium experiments.

The chief cause of poor approach to equilibrium in these cases is evident from the effusion data. The

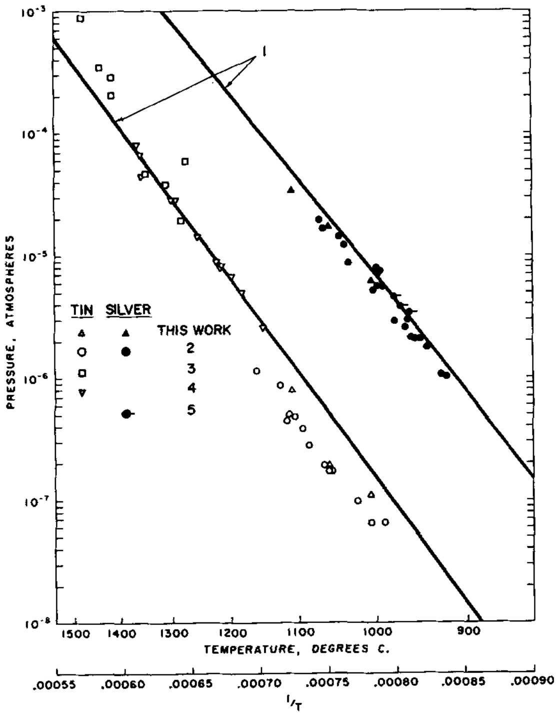

Fig. 4. Vapor pressures of silver and tin. 1, Third law extrapolations of previous data by *Stull and Sinke* (5); 2, *Harteck* (1); 3, L. Brewer and R. F. Porter, *J. Chem. Phys.*, 21, 2012 (1953); 4, A. W. Searcy and R. D. Freeman, *J. Am. Chem. Soc.*, 76, 5229 (1954); 5, C. L. McCabe and C. E. Birchenall, *AIME Trans.*, 197, 707 (1953).

average increases in the effusion rates on adding gallia to tin, gallium, and graphite were, respectively, 150-fold, 2000-fold, and an undetermined large factor. These compare to average increases of two to fourfold on adding quartz and magnesium oxide to gallium. If the reaction between the oxide and the metal involves mainly metal vapor rather than liquid metal, the ease of achieving equilibrium in the effusion cell will be related to the ratio of the equilibrium pressure from the reaction to the equilibrium metal vapor pressure. If this ratio is large, equilibrium will be difficult to achieve, especially as this ratio approaches the ratio of the metal surface area to the area of the effusion hole.

Reaction between metal vapor and the oxide would be expected to be the predominant reaction in the effusion cells because gaseous products formed at submerged sites where the liquid metal and oxide are in contact would have difficulty in escaping from under the head of molten metal at these low pressures. With the quartz and magnesium oxide added to the gallium, the increase in pressure was small enough that the gases in the effusion cell were probably at equilibrium.

Gershenzon and Mikulyak (9) reported that Frosch and Thurmond of Bell Telephone Laboratories, Inc. of Murray Hill, New Jersey, have measured gallium suboxide pressures of 0.2 mm at 800°C

Table III. Silver and tin vapor pressure data

	Ag		Sn	
°K	Effusion rate, mg/hr	Pressure, atm	Effusion rate, mg/hr	Pressure, atm
1280	2.38	6.1×10^{-6}	0.044	1.1×10^{-7}
1332	6.31	1.7×10^{-5}	0.076	1.9×10^{-7}
1383	14.5	3.9×10^{-5}	0.308	7.8×10^{-7}

Table IV. Values of $-\left[\frac{F^\circ_T - H^\circ_{298}}{T}\right]$ and $\Delta H^\circ_{f\,298}$ employed in calculations from Janaf Interim Thermochemical Tables (11) unless otherwise noted

	°K	$Si_{(c)}$	$H_{2(v)}$	$C_{(c)}$	$Al_2O_{3(c)}$	$Al_2O_{(v)}$	$SiO_{2(c)}$	$H_2O_{(v)}$
$-\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)$	700	5.912	33.153	2.166	18.549	64.730	13.579	47.406
	800	6.361	33.715	2.449	20.656	65.672	14.728	48.089
	900	6.795	34.250	2.736	22.533	66.584	15.879	48.749
	1000	7.212	34.758	3.020	24.434	67.459	16.999	49.382
	1100	7.610	35.240	3.300	26.261	68.295	18.064	49.991
	1200	7.989	35.696	3.573	28.012	69.093	19.077	50.575
	1300	8.352	36.130	3.839	29.689	69.855	20.041	51.136
	1400	8.698	36.543	4.098	31.295	70.582	20.961	51.675
	1500	9.028	36.937	4.348	32.835	71.276	21.840	52.196
	1600	9.345	37.314	4.591	34.311	71.940	22.681	52.698
$\Delta H^\circ_{f\,298}$		0	0	0	—400.4	—39.4	—209.9	—57.798

	°K	$SiO_{(v)}$	$MgO_{(c)}$	$Mg_{(v)}$	$Co_{(v)}$	$Ga_2O_{3(c)}$[1]	$SnO_{(v)}$[1]	$Ga_2O_{(v)}$[2]
$-\left(\frac{F^\circ_T - H^\circ_{298}}{T}\right)$	700	52.634	9.263	36.892	49.182	25.63	57.56	73.03
	800	53.257	10.130	37.291	49.759	27.38	58.26	74.07
	900	53.858	10.969	37.670	50.314	29.07	58.95	75.08
	1000	54.432	11.775	38.029	50.845	30.71	59.54	76.04
	1100	54.980	12.546	38.368	51.351	32.30	60.13	76.96
	1200	55.502	13.283	38.688	51.834	33.82	60.63	77.83
	1300	55.999	13.986	38.991	52.295	35.24	61.17	78.66
	1400	56.473	14.658	39.278	52.736	36.65	61.56	79.46
	1500	56.926	15.301	39.550	53.158	37.98	62.14	80.22
	1600	57.358	15.916	39.809	53.562	39.23	62.61	80.96
$\Delta H^\circ_{f\,298}$		—21.411	—143.7	—35.330	—26.417	—258.0 (12)	—1.0	—

[1] Calculated from $\Delta H^\circ_{f\,298}$ (12) and $\Delta F^\circ_{f\,T}$ and free energy function for the component elements (5).
[2] Estimated by method described in text.

and 10 mm at 1000°C for a 4-1M mixture of gallium and gallium suboxide. From Curve 3 in Fig. 3, the corresponding pressures calculated for this reaction are 0.091 mm and 8.6 mm. This good agreement supports the choice of —19.7 kcal/mole for the value of $\Delta H^\circ_{f\,298[Ga_2O_{(v)}]}$.

Vapor Pressures of Silver and Tin

In order to obtain an independent check on the effusion cell constants employed in this work, the vapor pressures of silver and tin were determined. These are given in Table III and are compared with literature values in Fig. 4. There is good agreement with the results of Harteck (1) who employed quartz cells. These values average 22% to 46% lower than the values chosen by Stull and Sinke (5) from data obtained mostly in graphite cells. It appears that diffusion through graphite cell walls was not considered in most of the earlier work.[1]

Sources of Thermodynamic Data

Except for the free energy functions for liquid and gaseous Ag, Sn, and Ga which were obtained from Stull and Sinke (5), all of the free energy functions and heats of formation employed are listed with their sources in Table IV.

Estimated values of the free energy functions for $Ga_2O_{(v)}$ are also listed in Table IV. This quantity is a function of heat capacities alone and, therefore, can be estimated for gases quite accurately from heat capacity data for molecules of similar structure and molecular weight. A value of 69.54 was estimated for $S^\circ_{298[Ga_2O_{(v)}]}$ from a correlation of molecular weights with values of S°_{298} for other triatomic gaseous molecules. Heat capacities for $Ga_2O_{(v)}$ above 298°K were taken to be the same as for $CTeS_{(v)}$ from the Bureau of Mines Bulletin 584 (13).

The described free energy functions were used to calculate the free energy function changes for the reaction at 100°K intervals. Free energy function changes for the desired temperatures were obtained by graphical interpolation.

Manuscript received June 28, 1961.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1962 JOURNAL.

REFERENCES

1. P. Harteck, *Z. physik. Chem.*, **134**, 1 (1928).
2. R. Speiser and H. L. Johnston, *J. Am. Chem. Soc.*, **75**, 1469 (1953).
3. S. Antkiw and V. H. Dibeler, *J. Chem. Phys.*, **21**, 1890 (1953).
4. C. N. Cochran, *Rev. Sci. Instr.*, **29**, 1135 (1958).
5. D. R. Stull and G. C. Sinke, "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D. C. (1956).
6. J. Drowart and R. E. Honig, *Bull soc. chim. Belges.*, **66**, 411 (1957).
7. D. A. R. Kay and J. Taylor, *Trans. Faraday Soc.*, **56**, 1372 (1960); J. D. Baird and J. Taylor, *Trans. Faraday Soc.*, **54**, 526 (1958).
8. W. D. Good, Bureau of Mines, Bartlesville, Oklahoma, Private communication.
9. M. Gershenzon and R. M. Mikulyak, *This Journal*, **108**, 548 (1961).
10. S. Fujishiro and N. A. Gokcen, *J. Phys. Chem.*, **65**, 161, (1961).
11. JANAF Interim Thermochemical Tables, Thermal Laboratory, Dow Chemical Company, Midland, Michigan, Dec. 31, 1960.
12. J. P. Coughlin, Bulletin 542, U. S. Bureau of Mines (1954).
13. K. K. Kelley, Bulletin 584, U. S. Bureau of Mines (1960).

---

[1] Fujishiro and Gokcen (10) found that the amount of titanium vapor permeating the walls of a cell made from a very dense, impervious graphite ranged from 45 to 77% of the total effusate in the 2383°-2593°K range.