Nickel-NiO Thermodynamic Cycle: Values of $\Delta G°$ and $\Delta H°$

Emile Rutner[1] **and Gerard L. Haury**
Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio 45433

The "best values" of the parameters in the vapor-pressure equations of solid and liquid nickel and the heat of vaporization of nickel are statistically deduced on the basis of all available data. Corrected estimates of the heat of vaporization of NiO(s) and heats of dissociation of NiO(g) and Ni_2(g) are obtained. "Best values" of maximum ionization cross sections useful in thermodynamic mass spectrometry are also reported.

There have been a number of determinations of the vapor pressures and the heats of vaporization of solid and liquid nickel (*3, 9, 16, 22, 28–31*). The range of values of these properties was rather large; therefore, a new determination of the heat of vaporization of solid nickel was undertaken, and these results were combined with the available data in the literature to obtain a "best value" of the heat of vaporization and vapor pressures by a statistical treatment. The critical evaluation of the available data was especially desirable since there appeared to be sufficient data in the literature to complete the following thermodynamic cycle, thus lending consistency to the values of the individual heats of reaction.

$$Ni(s) + \tfrac{1}{2}O_2(g) \rightarrow NiO(s) \tag{1}$$

$$NiO(s) \rightarrow NiO(g) \tag{2}$$

$$NiO(g) \rightarrow Ni(g) + O(g) \tag{3}$$

$$O(g) \rightarrow \tfrac{1}{2}O_2(g) \tag{4}$$

$$Ni(g) \rightarrow Ni(s) \tag{5}$$

In the process of examining and reducing the data in the literature, new estimates of values of the heats of dissociation of NiO(g) and Ni_2(g) were obtained by correcting the available data. Furthermore, during the examination of the mass-spectrometric techniques involved in one of the vapor-pressure determinations, best values of the ionization cross sections of the species H, O, Ni, Ag, and O_2 were deduced. These were then used to correct the available mass-spectrometric data on the pressure of the gaseous species generated by NiO(s) (*9*).

Experimental Methods and Results

The method used in determining the vapor pressure of nickel solid was the Langmuir (*23*) technique. The apparatus used is depicted in Figure 1 and consisted of an RF coil powered by a Sealometic Electronics inductance furnace Model 2000-20 kW operated at a frequency of 3 MHz. The coil, which was used to heat a cylindrical sample to a given temperature, was made of five turns of ¼-in. copper tubing and was 5.75-cm i.d. and 4.5-cm long.

The furnace was contained in a bell jar 15.25-cm i.d. × 28-cm high. The specimen was suspended inside the coil by means of 0.0127 cm in diameter tungsten wire, which was looped around the sample to form a harness. The two ends of the wire were hooked to an inconel wire 7.6 cm above the specimen, and the inconel wire, in turn, was hooked to a nylon thread hanging from the end of the electro-balance beam. The enclosure containing the balance and sample was evacuated to 10^{-5} torr. [Throughout this paper, torr = (101.325/760) kPa; atm = 101.325 kPa; cal_{th} = 4.184 J; eV = 96487 J mol^{-1}; cm^{-1} = 11.927 J mol^{-1}; T = K; Å = 10^{-8} cm; inch = 2.54 cm; minute = 60 sec; $R(cal_{th}\ mol^{-1}\ K^{-1})$.] The bell jar which formed the sample chamber was surrounded by a water jacket to cool it and to remove condensable gases. The same water system cooled the induction furnace and RF coil.

The weight of the sample was measured by a vacuum electro-balance (Cahn-type RH) which was monitored by a Hewlett-Packard Model 419A dc null voltmeter in conjunction with a Brown (Model 153) single-point recorder.

The specimen was a nickel cylinder 1.27-cm diam × 1.60-cm long of 99.95% purity supplied by the Gallend Schlesinger Chemical Co. The sample had a black body hole 0.159-cm i.d. × 0.635-cm deep. The temperature was obtained by means of an optical pyrometer which was calibrated against an NBS standard strip lamp at several temperatures between 1173 and 1873K (IPTS 1948). A calibration curve was obtained for the experimental arrangement used by placing a standard lamp in situ of the sample (Figure 1); corrections thus were made for radiant intensity losses owing to absorption and length of path between sample and pyrometer. The temperature calibration had a mean deviation of ±2.6K over the temperature range.

The sample was outgassed at 1673K for 15 min before heating to the desired temperature. The sample was then

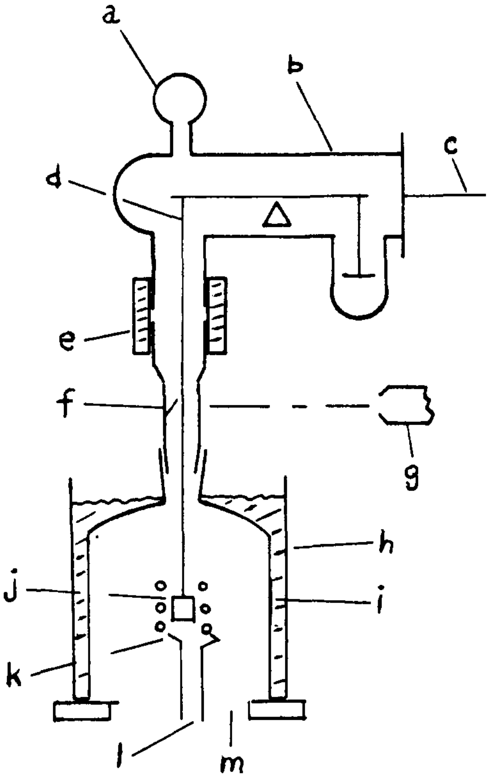

Figure 1. Experimental arrangement for determining rate of weight loss of nickel samples. (a) Vacuum gage, (b) microbalance, (c) microbalance readout, (d) sample suspension, (e) rubber bushing, (f) mirror, (g) optical pyrometer, (h) water jacket, (i) bell jar, (j) specimen, (k) induction coil, (l) power leads, (m) to vacuum pumps

---

[1] To whom correspondence should be addressed.

maintained at temperature until the weight loss rate became constant. The sample was weighed, then heated at temperature for a period of time to give an adequate weight loss. The weight loss in all the cases used in determining the final value of the heat of vaporization was large enough to limit the weighing error to 1% without significantly changing the surface area. The time at temperature was also large enough to minimize errors in the weight loss during the heating up and cooling down time periods. In the treatment of the data, the following relation was used to determine the vapor pressure from the mass loss rate per unit area (*23*).

$$(P/\text{atm}) = 2.255 \times 10^{-2}(\dot{m}/\text{g cm}^{-2}\ \text{sec}^{-1})\ (T)^{1/2}(M/\text{g mol}^{-1})^{-1/2} \qquad (6)$$

The heat of vaporization by the "second-law" method is obtained from the least-squares slope of the ln P vs. T^{-1} curve. The slope is assumed to be constant over the range, which implies that $[\Delta c_p/\text{cal}_{\text{th}}\ \text{mol}^{-1}\ \text{K}^{-1}]$ is zero. Therefore, the only point at which the heat of reaction is correct is at the mean inverse temperature. There are systematic errors in the heat of vaporization in assuming that the slope is constant over the whole temperature range; these errors will be discussed in conjunction with the statistical analysis given below. The data used to obtain a least-squares slope are given in Table I under ref. *36*. The value of $\Delta H_0°(\text{Ni, s} \rightarrow \text{v}) = 115.8 \pm 5.6\ \text{kcal}_{\text{th}}\ \text{mol}^{-1}$ was obtained from $\Delta H°(\text{Ni, s} \rightarrow \text{v, 1501}) = 114.0 \pm 5.5\ \text{kcal}_{\text{th}}\ \text{mol}^{-1}$ by utilizing the enthalpy tables of Hultgren et al. (*14*).

The "third-law" values of $\Delta H°(\text{Ni, s} \rightarrow \text{v, 298})$ were obtained from the following relation between the vapor pressure for reaction five and "free-energy functions" whose values are given by Hultgren et al. (*14*).

$$\Delta\{-[G° - H°(298)]\cdot T^{-1}, (\text{s} \rightarrow \text{v})\} + R \ln P\ (\text{atm}) = \Delta H°\{(298), (\text{s} \rightarrow \text{v})\} \cdot T^{-1} \qquad (7)$$

The values of $\Delta H°(298)$ were used to determine $\Delta H_0°$ by use of enthalpy tables (*14*). The correction was equal to $(-0.49\ \text{kcal}_{\text{th}}\ \text{mol}^{-1})$; Table II gives the values of $\Delta H°(298)$ obtained in conjunction with the vapor pressures for Rutner and Haury shown in Table I. The points which were omitted in the final determination varied more than 2-rms deviations from the mean value of $\Delta H°(298)$. The criteria for discarding data and discussion of errors are given below.

Statistical Evaluation of Available Data on Vapor Pressure of Nickel

The "best values" of the heat of vaporization of solid and liquid nickel and the parameters in the vapor-pressure equations over a limited temperature range

$$\ln P(\text{atm}) = A + BT^{-1} \qquad (8)$$

were determined by statistically weighing the available heats of vaporization and vapor pressures (*3, 9, 16, 22, 28–31*) and our data, Table I.

The first step in the evaluation process was an examination of the available information given by each author on the experimental techniques used. In the examination, cognizance was taken of methods of temperature measurements; condition of samples; weight-loss determination; consistencies between second- and third-law values of the heats of vaporization; and external consistencies of heats of vaporization.

In evaluating the significance of the consistencies between second- and third-law values of the heats of vaporization, in general, the "third-law" heats of vaporization are more consistent with external data than "second-law" heats of vaporization, and the individual deviations in "third-law" heats of vaporization are generally smaller than those of the second law. There is one obvious reason for this when it is noted that the percentage errors in ΔT can be much larger than those in the absolute value of T. Furthermore, in the use of the third-law method, the errors in the term (T ln P) tend to cancel since ln $P \sim -T^{-1}$ and (T ln P) is approximately constant for small changes in temperature.

The experimental technique of Rutner and Haury has been discussed above in the Experimental section. The lack of consistency between the second- and third-law values of the heats of vaporization have also been discussed above.

The data of Nesmeyanov and Tik-Mang (*29–31*) were evaluated but not utilized because the vapor pressures which were determined by measuring the weight-loss rate

Table I. Reported Vapor Pressures of Nickel Considered in Determining Best Values of $\Delta H_0°$; A, B (Equation 8) by Second- and Third-Law Methods

T, K	P, atm	T, K	P, atm	T, K	P, atm
Rutner and Haury (*36*)		Johnston and Marshall (*16*)		Langmuir (*23*)^a	
1393^{b,c}	8.00×10^{-9}	1583	4.63×10^{-7}	1318	3.20×10^{-9}
1345^c	9.82×10^{-10}	1308	5.61×10^{-10}	1409	6.67×10^{-8}
1610	5.55×10^{-7}	1307	6.00×10^{-10}	1532	4.34×10^{-7}
1546	8.27×10^{-8}	1397	7.24×10^{-9}	1544	5.07×10^{-7}
1447	5.02×10^{-8}	1397^c	8.16×10^{-9}	1604^c	4.38×10^{-5}
1563	4.69×10^{-7}	1387	5.70×10^{-9}		
1558	2.49×10^{-7}	1415	1.09×10^{-8}	Nesmeyanov and Tik-Mang (*29–31*)^d	
1562	1.62×10^{-7}	1465	3.72×10^{-8}		
1658	3.21×10^{-6}	1507	9.92×10^{-8}	1525	1.54×10^{-4}
1648	8.18×10^{-7}	1576	4.53×10^{-7}	1483	6.08×10^{-5}
1277^b	5.38×10^{-9}	1578	4.55×10^{-7}	1478	6.17×10^{-5}
1428	2.81×10^{-9}	1397^b	8.16×10^{-9}	1443	3.07×10^{-5}
1403	2.62×10^{-9}	1466^b	4.33×10^{-8}	1439	2.69×10^{-5}
1373	6.78×10^{-10}			1401	1.29×10^{-5}
1363	1.15×10^{-9}	Grimley et al. (*9*)^e		1411	1.40×10^{-5}
1433	2.99×10^{-9}	1575^b	2.71×10^{-7}	1365	4.84×10^{-6}
1523	5.63×10^{-8}	1596^b	4.47×10^{-7}	1320	2.15×10^{-6}
1488	2.67×10^{-8}	1606	5.44×10^{-7}	1550^c	2.27×10^{-4}
1458	1.33×10^{-8}	1624	8.50×10^{-7}	1371^b	4.65×10^{-6}
1613	4.17×10^{-8}	1625	8.50×10^{-7}		
1613	4.51×10^{-7}	1630	9.44×10^{-7}	Morris et al. (*28*)^f	
1593	3.66×10^{-7}	1646	1.39×10^{-6}	1895	5.09×10^{-5}
1563	1.13×10^{-7}	1651	1.53×10^{-6}	1894	5.08×10^{-5}
1543	1.19×10^{-7}	1657	1.69×10^{-6}	1885	4.37×10^{-5}
1353	4.35×10^{-10}	1659	1.71×10^{-6}	1816	1.68×10^{-5}
1483	3.42×10^{-8}	1673	2.18×10^{-6}	1876	4.03×10^{-5}
1233^{b,c}	3.42×10^{-10}	1673	2.25×10^{-6}	1868	3.47×10^{-5}
1513^{b,c}	3.88×10^{-7}	1679	2.51×10^{-6}	1853	2.91×10^{-5}
		1684	2.80×10^{-6}	1848	2.68×10^{-5}
Bryce (*3*)^g		1679	2.50×10^{-6}	1842	2.51×10^{-5}
1273	3.22×10^{-10}	1684	2.82×10^{-6}	1839	2.34×10^{-5}
1252	1.29×10^{-10}	1707	4.12×10^{-6}	1836	2.30×10^{-5}
1423	1.84×10^{-8}	1709	4.31×10^{-6}	1828	1.99×10^{-5}
1391	4.86×10^{-9}	1587^c	4.42×10^{-7}	1848	2.66×10^{-5}
1341	1.45×10^{-9}			1860	3.20×10^{-5}
1324	1.38×10^{-9}			1821	1.79×10^{-5}
1299	9.88×10^{-10}			1862^c	3.37×10^{-5}

Data points were omitted whose deviations were greater than 2 σ (rms deviation) from second-law and third-law best values. [a] Not used in composite third-law determinations. [b] Eliminated from second-law individual determination. [c] Eliminated from third-law individual determination. [d] Not used in final composite determinations. [e] These data have been corrected for errors in cross sections. [f] Liquid-phase vaporization corrected for heat of fusion. Not used to determine best value of A by second or third law. [g] All points reported included.

from a Knudsen cell were 10^3 times larger than those previously and subsequently reported; thus, the second- and third-law values of the constant to A and B in Equation 5 were different markedly from the best composite values. (See Table IV, for example.)

Johnston and Marshall (*16*) determined the vapor pressure of nickel by a free vaporization or Langmuir technique. They determined the temperature by sighting on a black body hole in a sample which was doughnut shaped. They made brightness intensity corrections for the absorption of radiation by the windows. The shape of the sample introduced an error owing to condensation of material on the inside surface of the doughnut hole; a correction was made for this error. The weight loss was determined by the use of a sensitive balance. Although the authors claim an error of ±5% in the pressures measured, the data require some interpretation since there appears to be an uncertainty in the area of the condensation surface. The data presented involved an error of ±5% in the weighing and ±5K in the temperature. The error in the pressure is not necessarily the same as the error in the weighing, since the weight-loss rate may be significantly affected by errors in corrections made for recondensation on the sample.

Langmuir et al. (*22*) reported measurements of the vapor pressure by a free evaporation from a nickel filament. The temperature was measured with a pyrometer and an emissivity of 0.36 was assumed for the nickel at temperature. This assumption led to an error in the determination of the temperature. There was another error owing to determination of the length of wire at temperature. Although estimates on the limits of these errors could be determined, the data herein fall out of the statistical limits which were set for use of the data in obtaining the best values of the heats of vaporization and vapor pressures by the third-law method and, therefore, were omitted from these determinations.

Table II. Third-Law Values ΔH° (Ni, s → v, 298) Obtained by Rutner and Haury (*36*)

(T, K)	ΔH° (298), cal_{th} mol^{-1}
1345	102.92
1428	106.16
1546	97.75[a]
1447	99.25
1558	101.72
1562	103.33
1563	100.06
1610	102.46
1648	104.17
1658	99.65
1363	103.86
1353	105.74
1433	106.37
1483	102.83
1543	102.46
1523	104.00
1488	103.86
1458	103.84
1613	103.57
1613	103.34
1593	102.74
1563	104.50
1403	105.17
1373	106.03
1393	100.72[b]
1233	97.09[a,b]
1277	99.36[b]
1513	97.53[a,b]

[a] Eliminated from second-law determination of ΔH_0°. [b] Eliminated from third-law determination of ΔH_0°.

Morris et al. (*28*) measured the vapor pressures of liquid nickel by a gas transport method utilizing an inert gas, helium, as the transport gas. The metal vapor was condensed onto the inner surface of the gas outlet tube. The gas flow rates were determined by a wet gas meter. The temperature was controlled to ±5K and was determined by means of an optical pyrometer. Corrections for absorption of the radiation by the windows were made. A colorimetric method was used to determine the weight of nickel deposited by the gas stream. The possible errors in the spectroscopic determination of the nickel carried by the gas were not evaluated. The error in the volume of the gas gives a proportional percentage error in the vapor pressure. The probable error in the gas volume was less than 1%.

Bryce (*3*) determined the vapor pressure of nickel by the vaporization of a filament by use of a target to catch the nickel vapor. The nickel condensed on the target was determined by a chemical technique. No further data are available on the technique.

Grimley et al. (*9*) determined the vapor pressure of nickel during the course of a mass-spectrometric investigation of the vaporization behavior of nickel oxide by combining the Knudsen cell effusion technique with a mass spectrometer. The temperature was determined by sighting on black body holes in the Knudsen cell. There was some evidence that a reaction took place in the Knudsen cell which was made from aluminum oxide. There is no evidence that this reaction affected the measured vapor pressure or the observed heat of vaporization of nickel.

Grimley et al. (*9*) used incorrect ionization cross sections for the ionization of the molecular and atomic species involved. The error in the ionization cross section of silver, the calibrating substance, introduced an error in the geometric factor defining the number of atoms which are in the volume defined by the electron beam. The error in the relative ionization cross section of Ni(g) and Ag(g) caused an error in the observed vapor pressure of Ni(s). The reported vapor pressures of Ni(s) were corrected by us by use of the following relation:

$$\ln\left[\sigma_2(\text{Ni})/\sigma_1(\text{Ni})\right]\left[\sigma_1(\text{Ag})/\sigma_2(\text{Ag})\right] = \ln\left[P_1(\text{Ni})/P_2(\text{Ni})\right] \quad (9)$$

where σ is the ionization cross section of the species in brackets, and P is the pressure of the species. The subscript 1 refers to the original data of Grimley et al. and subscript 2 refers to the corrected values. The resulting correction was $P_2(\text{Ni}) = 0.78\ P_1(\text{Ni})$.

"Best Value" Obtained by "Second Law" of ΔH_0°; A and B for Equation 8

In the "second-law" treatments of the experimental data, the data from each laboratory, i, were fitted by a least-squares method to Equation 8. In Equation 8, $B = [\Delta H^\circ(\bar{T})]\cdot R^{-1}$, and $\Delta H^\circ(\bar{T})$ is the heat of vaporization at the mean inverse temperature: $\bar{T} = [n_i^{-1}\Sigma T_j^{-1}]^{-1}$, where T_j is the temperature of the jth data point, and n_i are the number of data points reported by the ith laboratory.

All reported pressures having a deviation from the calculated values of the pressure which were greater than 2 σ (σ = rms deviation) were eliminated from the originally reported data in determining the least-squares value of the slope.

After having determined the least-squares value of the individual $\Delta H_i^\circ(\bar{T}_i)$, these quantities were then used to determine the individual $(\Delta H_0{}^\circ)_i$ by use of the enthalpy tables of Hultgren et al. (*14*). These tables round off to identical values to the second decimal place with other available tables (*18, 37, 41*). The list of data used is given in Table I.

Before applying the "least-squares" treatment to the data of the individual laboratories, the data were examined for signs of "systematic errors" or "nonrandom errors" by arranging the deviations of the pressures in ascending order and plotting the deviations on probability paper. In all cases, the data formed several groupings, each of which could be fitted with a straight line. The deviations of the plots from a single straight line were not limited to the end points, thus indicating that the errors were "nonrandom" (*25*).

The "best values" of the parameters *A* and *B* of Equation 8 for each *individual set of data* were determined by successively eliminating data points whose deviations between the measured values of the pressure and calculated values were greater than 2 σ (rms deviation). In some cases more than one recalculation was necessary, thus further indicating a lack of statistical homogeneity in the data. (Refer to Table III.)

The *composite* "best values" of *A* and *B* were obtained by utilizing the statistical treatment described in ref. *26* to determine the applicable weighing factors in averaging the individual values of $(\Delta H_0{}^\circ)_i$ derived by the least-squares treatment. The treatment is an attempt to weigh the effect of deviations between each laboratory's "best values" and that of the deviations in the "within the individual laboratory" results. In applying the technique (*26*), it is necessary to note that the statistical number of degrees of freedom for each laboratory is $(n_i - 2)$ in determining the best value of the slope. All other quantities and the procedures required for the determination of the composite best values of *B* and *A* for Equation 8 are given in ref. *26* (Table I).

The composite "best value" of the heat of vaporization of nickel solid, which was obtained by utilizing the statistical method of ref. *15* was: $\Delta H_0{}^\circ(\text{Ni}, s \rightarrow v) = 102.9 \pm 4.2$ ($\text{kcal}_{\text{th}}\ \text{mol}^{-1}$).

It was also of interest to obtain the value of *B* for a given temperature range so that Equation 8 could be used to calculate vapor pressures. Since the data utilized cover the temperature range 1273–1709K, a value of *B* at the midpoint of this range was calculated. Note that there is a difference in specifying the average temperature for the range, 1491K, as the midpoint, and the average temperature that is derived from the reduction of a set of data by the least-squares technique. The value of $B(1491) = \Delta H^\circ(1491) \cdot R^{-1}$ was obtained by using the enthalpy tables (*10*) to correct $\Delta H_0{}^\circ$ to $\Delta H^\circ(1491) = 101.1 \pm 4.3\ \text{kcal}_{\text{th}}\ \text{mol}^{-1}$.

Table III. Quantities Used in Determining Composite Second-Law "Best Value" of $\Delta H_0{}^\circ$; and *B* and *A* (Equation 8) for Vaporization of Solid Nickel

Ref	No.[a] of data points, n_i	$\Delta H_0{}^\circ$, $\text{kcal}_{\text{th}}\ \text{mol}^{-1}$	Variance,[b] $\sigma_i{}^2\ [\Delta H^\circ]$	*A*	Variance,[b] $\sigma_i{}^2$ (*A*)
[c]	24	115.83	31.36	27.861	3.389
9	18	112.36	1.56	26.735	0.144
16	10	102.21	0.34	24.092	0.0433
3	7	93.99	58.69	21.354	8.451
22	5	89.36	48.16	20.955	5.688
28	15	103.10	1.12	[d]	[d]

[a] Number of data points after elimination of those deviating more than 2 σ (rms deviation) reported by laboratory *i*. [b] Statistical degrees of freedom equal $(n_i - 2)$ for each determination. [c] See Experimental section. [d] Liquid nickel, this value not used in averaging.

There is a maximum error of 0.65 kcal_{th} over the temperature range introduced by assuming that ΔH° is constant over the range. The error of 0.65 kcal_{th} is the systematic error at the end points of the range; to a good approximation, the average total error over the range may be estimated as ±4.6 kcal. Therefore, the average "second-law" value $\overline{\Delta H^\circ}$ (1273–1709K) is given as $101.1 \pm 4.6\ \text{kcal}_{\text{th}}\ \text{mol}^{-1}$, and the value of $B = 50884 \pm 2466$K over the temperature range.

An estimate of the intercept *A* was also made by use of the same statistical treatment which was used in deriving the value of *B*. In deriving the value *A*, however, the data of Morris et al. (*28*) were omitted since these data refer to the liquid vaporization. Furthermore, since the parameters in Equation 8 must relate to a temperature range which does not involve a discontinuity in the parameters, such as caused by a phase change, two values of *A* and *B* were calculated which can be used to calculate the vapor pressure over the whole temperature range for which data are available.

The "best values" from the second-law determinations for *A* and *B* for both the solid and liquid ranges are given in Equations 10–13.

For the reaction

$$\text{Ni(s)} \rightarrow \text{Ni(g)}\ \Delta H^\circ(1491) = 101.1 \pm 4.3\ \text{kcal}_{\text{th}}\ \text{mol}^{-1} \tag{10}$$

and the vapor pressure over the temperature range 1273–1709K is:

$$\ln P(\text{Ni, s, atm}) = 17.63 \pm 1.39 - (50884 \pm 2466) \cdot T^{-1} \tag{11}$$

For reaction:

$$\text{Ni(l)} \rightarrow \text{Ni(g)}\ \Delta H^\circ(1855) = 95.91 \pm 1.06\ \text{kcal}_{\text{th}}\ \text{mol}^{-1} \tag{12}$$

there is only one value of ΔH° which was obtained from data in ref. *8*. These data were statistically treated to eliminate pressure data points which deviated more than 2 σ (rms deviation) from the calculated values. This treatment yielded the following values of $A = 15.589$ and $B = 48271$K. These values compare with the values of $A = 15.681$ and $B = 48432$K reported in ref. *8*. The best "second-law" equation for the vapor pressure of liquid nickel in the temperature range 1816–1895K is:

$$\ln P\ (\text{Ni, l, atm}) = 15.59 \pm 0.29 - (48271 \pm 533) \cdot T^{-1} \tag{13}$$

In subsequent discussions covering the third-law "best values," relations between *A* and the free-energy functions will be discussed.

Third-Law Determinations of Best Values of *B*, *A*, and $\Delta H_0{}^\circ$

Third-law determinations of the "best values" of the quantities *B*, *A*, and $\Delta H_0{}^\circ$ can be made by utilizing the expressions for the free-energy functions and the values of these functions given in ref. *14* and the data reported in ref. *3, 9, 16, 22, and 28–31*. The data in ref. *29–31* were omitted because they were inconsistent with other data, as noted above. The data in ref. *22* were also omitted because the value of $\Delta H_0{}^\circ$ obtained from this set of data deviated by more than 2 σ from the average $\Delta H_0°$ obtained by simply statistically weighing the values of each set of data by the number of data points reported by each laboratory.

This statistical test is crude, since it assumes that the data are statistically homogeneous, but it is useful in setting an upper limit to the variance of the sets of data to be used in subsequent statistical averaging. The reason that only an upper bound of the variance was used in determining what data to consider or retain within the individual sets and the composite data was due to the fact that the data were statistically too inhomogeneous to treat by the χ^2 test which utilizes both upper and lower bound.

To compare the equation for ln P in the temperature range 1273–1709K with that obtained by means of the "second law" as noted above, it is necessary to compare equations for ln P used to obtain "third-law" values of $\Delta H°$ with that used to obtain the "second-law" values of this quantity. In the use of the second law, the slope of the line ln P vs. T^{-1} is equated to the quantity $[\Delta H°(\bar{T})]\cdot R$, where $\bar{T}$ is the temperature corresponding to the mean inverse temperature as noted above. The equation used to obtain the value of $\Delta H°(298)$ by the third law is as follows:

$$R \ln P(\text{atm}) = \sum_{g,s}(-1)^n([-(G° - H°(298))T^{-1}] - (H°(298))T^{-1}) \quad (14)$$

In Equation 14, n equals 0 for the functions corresponding to products of the reaction and equals 1 for those corresponding to reactants. The summation is taken of the thermodynamic function of gas and solid. To convert Equation 14 to the "second-law" form or to Equation 8, the quantity $\Sigma_{g,s}\ (-1)^n(H°(\bar{T}) - H°(298))\cdot T^{-1}$, must be subtracted from and added to the righthand side of the equation, resulting in Equation 15:

$$R \ln P = \sum_{g,s}(-1)^n[-(G° - H°(\bar{T}))T^{-1}] - (\Delta H°(\bar{T}))T^{-1} \quad (15)$$

As will be shown, the quantity $[(G° - H°(298))\cdot T^{-1}]$ is almost constant over the temperature range of interest so that its average can be taken as the constant A, which is given by Equation 16 when the pressure is expressed as P(atm)

$$A = \sum_{g,s}(-1)^n[-(G° - H°(298))(R\bar{T})^{-1}] + (R\bar{T})^{-1}\int_{298}^{\bar{T}} \sum_{g,s}(-1)^n c_p (\text{cal}_{\text{th}}\,\text{K}^{-1}\,\text{mol}^{-1})dT \quad (16)$$

In Equation 16, the specific heat, c_p, is a function of temperature. The slope B is given by

$$B = -\Delta H°(298)\cdot R^{-1} - R^{-1}\int_{298}^{\bar{T}} \sum_{g,s}(-1)^n c_p dT \quad (17)$$

All third-law data were reduced by using the values of the free-energy function given in ref. *14*.

An estimate of the error in the tabulated free-energy functions is limited to assuming that the error is that reported by Kelly (*18*) for enthalpies in this temperature range. This error is 0.3%. However, additional errors in A arise owing to the fact that the quantity $\Sigma_{g,s} - [(-1)^n(G° - H°(298))\cdot T^{-1}]$ is not a constant over the temperature range. The error owing to the variation of this quantity has been evaluated by finding its mean value for all determinations used, and evaluating the mean deviation; to this deviation was added the estimated average error resulting from assuming that $\Delta H°(T)$ equals $\Delta H°(\bar{T})$ over the whole temperature range.

The mean value of A for the temperature range of interest to us is that at the temperature $\bar{T}$ = 1535K, which is the inverse mean temperature. This method of obtaining the mean temperature is consistent with the method of averaging the free-energy functions, which are weighed by the quantity T^{-1}. The error arising in the use of the average free-energy function over the temperature range 1250–1710K is not random but can be expressed as a maximum limit of the error at the end points of the range.

The maximum error over the range including the 0.3% error in the free-energy functions is 1.5%, and the average deviation is 0.7%. If it is wrongly assumed that the errors are random and the rms deviation is calculated, then an estimated error of 0.8% is obtained. The above is a statement of errors which arise in the use of the average value of A = 16.87 at $\bar{T}$ = 1535K. The value of $\Delta H°(1535)$ = 99.5 ± 0.6 $\text{kcal}_{\text{th}}\ \text{mol}^{-1}$, and B = 50060 ± 500K. The best value $\Delta H_0°$ = 101.5 ± 0.6 $\text{kcal}_{\text{th}}\ \text{mol}^{-1}$. This value of $\Delta H_0°$ is more reliable than the "second-law" value of 102.9 ± 4.2 $\text{kcal}_{\text{th}}\ \text{mol}^{-1}$, even though they are nearly equal. The near equality appears to be fortuitous when one considers the range of the values of $\Delta H°(298)$ used in the two determinations.

The best "third-law equation" for the vapor pressure of solid nickel in the temperature range 1250–1710K utilizing the data in Table IV is as follows:

$$\ln P(\text{Ni, s, atm}) = 16.87 \pm 0.35 - (50600 \pm 500\text{K})(T)^{-1} \quad (18)$$

The third-law parameters of Equation 8 can also be determined for liquid nickel from the limited amount of data available (*28*). In the temperature range 1816–1895K, the third-law equation for the vapor pressure of liquid nickel is given by:

$$\ln P(\text{Ni, l, atm}) = 15.35 \pm 0.05 - (47775 \pm 210)(T)^{-1} \quad (19)$$

Since there are differences between the statistical treatments of data reported herein and that reported by Mandel and Paule (*26, 33*), a discussion of these differences is in order. The differences in the statistical treatments arise from the fact that the data available on the vapor pressure of nickel lack statistical homogeneity; thus, a composite value of the second- and third-law heats of vaporization could not be generated by simply treating all the data as a single set of data and obtaining a "best value."

Table IV. Third-Law Values of $\Delta H_0°$ Used to Calculate "Best Third-Law Values" for Ni(s) → Ni(g)

Ref	n_i[a]	$\Delta H_0°$, $\text{kcal}_{\text{th}}\ \text{mol}^{-1}$	Variance, $\sigma_i^2\ (\Delta H°)$
[b]	25	102.63	4.368
9	16	101.29	0.0169
16	12	100.74	0.04
3	7	100.28	0.7056
28	16	102.12	0.0049
29–31[c]	10	73.60	0.4356
21[c]	5	96.76	2.103
Best value		101.45	0.38

[a] n_i, number of determinations used after eliminating those with deviation >2 σ. [b] Experimental section and ref. *36*. [c] Not used in determining final value of $\Delta H_0°$.

The treatment which was used takes into account the nonhomogeneity of the data by statistically weighing the results of the individual laboratories which were used in generating an over all 'best value." The statistical test used for rejecting data in this paper is a deviation of the observed data of more than 2 σ (rms deviation). Paule and Mandel (*33*) used an *F* test which, in essence, put limits on the probability between 0.975 and 0.025 on the validity of the data they used. Although a 2 σ error limit does not take into account the number of degrees of freedom for each curve in setting error limits, it does give a convenient limit to the maximum deviation to be tolerated which has been used by other authors (*6, 8*).

The probability for the value of t (deviation/σ) > 2 (*8*) was between 5 and 15% with a large proportion of the cases being between 5 and 10%. Therefore, in general, this validity limit is not inconsistent with the other statistical treatments that were done. With continued elimination of data points whose deviations are greater than 2 σ, there is a reduction in the number of statistical degrees of freedom and the probability that a given value will fall outside of the 2 σ limit changes. By definition, the homogeneity of a given set of data (a measure of self-consistency) is measured by values of t = (deviation/σ).

Heat of Vaporization of NiO(s)

To complete the cycle, the value of the heat of vaporization of NiO(s) was required. The only available information on the heat of vaporization and the partial pressure of NiO(g) is that reported by Grimley et al. (*9*) and Johnston and Marshall (*16*). Johnston and Marshall (*16*) determined the vapor pressure of NiO(s) by determining the weight loss of an oxide coated sample of nickel. They noted that there was difficulty in accounting for the fraction of weight loss owing to nickel. Therefore, these data were disregarded.

The data of Grimley et al. (*9*) were obtained by use of a mass spectrometer, and as noted above, corrections are required to the vapor pressures reported owing to errors in cross sections of the species involved and errors in the thermodynamic functions used for the species NiO(g).

The errors in the cross sections resulted in the following corrections: the observed vapor pressure, P_1(NiO) $\times$ 0.64 = P_2(NiO), where P_2 is the corrected pressure.

Since the best value for the heat of vaporization was that obtained by the third-law method, estimates of the free-energy functions of NiO(g) were required. The relations used for calculating the free-energy functions were those given in the JANAF Tables (*15*). These relations are the same as those given by Herzberg (*11*) (Chapter V, Equations V, 79, and V, 83) and all preceding applicable relations in this chapter. The values and estimated errors of the required quantities which were used are given in Table V.

In evaluating the electronic partition function, it was necessary to determine the nature of electronic ground state of NiO. In previous reported guesses of the ground state configuration, Johnston and Marshall (*16*) considered the effect of the degeneracy, which they equated to the multiplicity, on the value of $\Delta H_0°$ for Reaction 2. Although they favored designating the ground state as $^3\Sigma^-$, they noted the differences between the value of $\Delta H_0°(q = 1)$ and the values of $\Delta H_0°(q \neq 1)$, where q is the degeneracy of the ground state. The differences were as follows: $[\Delta H_0°(q = 3) - \Delta H_0°(q = 1)] = 3266$ cal$_{\text{th}}$ mol^{-1} and $[\Delta H_0°(q = 10) - \Delta H_0°(q = 1)] = 6846$ cal$_{\text{th}}$ mol^{-1}.

Johnston and Marshall (*16*) also estimated the interatomic distance as 1.65×10^{-8} cm, which led to a value of the rotational constant $B = 0.50$ cm^{-1}. This value differs significantly from that reported by Huldt and Lagerquest (0.41 cm^{-1}) (*13*). They (*16*) also estimated the electronic ground state vibrational frequency as 700 cm^{-1} as compared to 615 cm^{-1} observed by Mallet and Rosen (*24*). Brewer and Chandraschrakaraish (*2*) reported a set of free-energy functions for NiO(g) based on the assumption that NiO was ionic and that Ni^{2+} species determined the electronic degeneracy. They also estimated other spectroscopic constants. The data reported in this set of tables were used by Grimley et al. (*9*).

In view of the uncertainty in the electronic ground state of the NiO(g), an attempt was made in our calculations to estimate the extent of the ionic character of the NiO(g) molecule. This is most easily done by the use of the relation for ionicity given by Pauling (*34*). The ionicity, Δ, is measured by the following relation

$$\Delta = \tfrac{1}{2}D_0°(O_2) + \tfrac{1}{2}D_0°(Ni_2) - D_0°(NiO) \qquad (20)$$

where $D°$ is the dissociation energy. The value $D_0°(O_2)$ used in this relation is 66.5 kcal$_{\text{th}}$ mol^{-1} and is equal to dissociation energy of two single (O—O) bonds. The heat of dissociation used for the Ni$_2$ molecule is that obtained from our correction (*36*) of Kant's (*17*) data, which is discussed below, and is given by $D_0°[Ni_2(g)] = 61$ kcal$_{\text{th}}$ mol^{-1}. The value of $D_0°[NiO(g)] = 85$ kcal$_{\text{th}}$ mol^{-1} (*9*) used in this estimate was that available before we had enough data to complete the cycle shown in Equations 1-5. Upon completion of our calculation, the value obtained was $D_0°[NiO(g)] = 92.7$ kcal$_{\text{th}}$ mol^{-1}. The value of $D_0°[NiO(g)] = 85$ kcal$_{\text{th}}$ mol^{-1} yields a value of Δ = 21 kcal$_{\text{th}}$ mol^{-1}. The value of $D_0°[NiO(g)] = 92.7$ kcal$_{\text{th}}$ mol^{-1} yields a value of Δ = 13 kcal$_{\text{th}}$ mol^{-1}. Thus, the ionicity is small; therefore, the molecule NiO(g) is probably covalent.

Further evidence that the molecule NiO(g) is not ionic is based on the large difference between the electron af-

Table V. Free-Energy Functions of NiO(g) — $[G° - H_0°][T]^{-1}$

T, K	Rotation + translation,[a] cal$_{\text{th}}$ mol^{-1} K^{-1}	Vibration,[b] cal$_{\text{th}}$ mol^{-1} K^{-1}	Electronic,[a] cal$_{\text{th}}$ mol^{-1} K^{-1}	Total, cal$_{\text{th}}$ mol^{-1} K^{-1}
100	36.66	0.00	0	36.66
200	43.48	0.02		43.50
298.16	46.24	0.11		46.35
300	46.30	0.12		46.42
400	48.30	0.23		48.53
500	49.85	0.37		50.22
600	51.12	0.52		51.64
700	52.19	0.66		52.85
800	53.12	0.80		53.92
900	53.94	0.93		54.87
1000	54.67	1.06		55.73
1100	55.33	1.18		56.51
1200	55.94	1.29		57.23
1300	56.50	1.40		57.90
1400	57.01	1.51		58.52
1500	57.49	1.61		59.10
1600	57.94	1.70		59.64
1700	58.36	1.79		60.15
1800	58.76	1.88		60.64
1900	59.13	1.96		61.09
2000	59.49	2.05		61.54

[a] Electronic levels: $V_{el} = 12725$ and 16447 cm^{-1} (*24*). Rotational constant $B = 0.41 \pm 0.02$ (*13*). [b] Vibrational frequency $\omega = 615$ cm^{-1} (*24*).

finity $E(O)$ of the O atom for two electrons to form $[O^{2-}]$ and ionization potential of Ni, $I(Ni)$ atom to form $[Ni^{2+}]$. The sum of the first two ionization potentials of Ni is [7.61 + 18.2 = 25.81 eV] (*40*), and the sum of the electron affinities of O atom to form (O^{2-}) is [1.465 + zero = 1.465 eV] (*1, 42*). The difference between these two sums is then 24.34 eV, which is too large to form a stable ionic species. Furthermore, in examining the possible stability of $[Ni^{+}O^{-}]$ molecules, we find that differences between the first ionization potential of Ni which equals 7.61 eV and the electron affinity of O to form $[O^{-}]$ which is 1.465 eV, equals 6.145 eV. This difference is still too large to form a stable ionic molecular species. As an example of a stable molecular-ionic species, we note the molecule $[Na^{+}Cl^{-}]$, for which the difference $[I(Na) - E(Cl)] = 1.4$ eV (*12*).

Table VI. Corrected Pressures of NiO (g) Data (*3*) and Third-Law Heats of Vaporization: NiO(s) → NiO(g)[a]

T, K	P, atm	$\Delta H_0°$, kcal mol^{-1}
1575	28.59×10^{-10}	125.35
1587	56.92×10^{-10}	124.09
1596	53.46×10^{-10}	124.97
1606	8.52×10^{-9}	124.22
1624	10.90×10^{-9}	124.76
1625	11.35×10^{-9}	124.70
1630	13.91×10^{-9}	124.40
1646	20.70×10^{-9}	125.16
1651	23.53×10^{-9}	124.20
1657	24.68×10^{-9}	124.32
1659	28.52×10^{-9}	124.14
1673	37.82×10^{-9}	124.20
1673	36.22×10^{-9}	124.35
1679	42.18×10^{-9}	124.30
1679	46.86×10^{-9}	123.93
1684	45.26×10^{-9}	124.38
1684	47.62×10^{-9}	124.21
1707	7.69×10^{-8}	124.20
1709	51.92×10^{-9}	125.68[b]

[a] Pressures = 0.641 × pressures reported in ref. *9*. [b] Omitted from final determination of $\Delta H°$ deviation $>2\ \sigma$ (rms deviation.)

Table VII. Data Used to Calculate D° by Means of Equation 1 (*17*)

Definition and term	Value
γ, product of ionization cross section and electron multiplier efficiency $[\gamma(Ni_2)][\gamma(Ni)]^{-1}$	1[a]
M, molecular weight	
M_1, atomic weight of monomer, i.e., Ni	58.71 g mol^{-1}
Q_{el} electronic partition function	
Q_{el} (Ni_2), dimer	1[b]
Q_{el} (Ni), atom[c,d]	$9 + 7 \exp - [1917][T]^{-1}$ $+5 \exp - [3191][T]^{-1}$ $+7 \exp - [2948][T]^{-1}$ $+5 \exp - [1267][T]^{-1}$ $+3 \exp - [2466][T]^{-1}$ $+5 \exp - [4909][T]^{-1}$
r, Radius of diatomic molecule	2.30 A[a,f]
Q_v,[a,e] vibration partition function vibrational partition function of (Ni_2)	$[1 - \exp - (467.7)(T)^{-1}]^{-1}$
Constant in Equation 1 (*17*)	3.2771; 2.8247[a]

[a] Value given in ref. *17*. [b] This value of Q_{el} $(Ni_2) = 1$ is obtained by assuming that the ground state of (Ni_2) is $^1\Sigma$. This differs from the assumption in ref. *17*. The choice of the $^1\Sigma$/(gs) is based on the possible electronic configurations of Ni_2 (*12b*). [c] Ref. *17* has a typographical error in this expression. [d] The electronic levels (cm^{-1}) and their degeneracies of the nickel atom which contribute to the partition function are as follows: 0.0 (9), 204.8 (7), 879.8 (5), 1332.2 (7), 1713.1 (3), 2216.5 (5), 3409.9 (5) (*27*). [e] The vibrational frequency of Ni_2 was assumed to be 325 cm^{-1}. The value was obtained by taking 1.25 × Debye frequency of the solid as in ref. 17. [f] Sum of covalent radii. Atomic radius Ni = 1.154 Å (*34b*).

The above evidence led to the assumption that NiO(g) was a stable covalent molecule of ground electronic state $^1\Sigma$. The other spectroscopic data for this molecule are given in Table V. The corrected values of the partial pressure of NiO(g) and the heats of vaporization by the third-law method are given in Table VI. The free-energy functions of NiO(s), which were used in obtaining $\Delta H_0°$ by the third-law method, were those reported by Wickes and Block (*41*) corrected to (O/K) by subtracting the enthalpy difference $[H°(298.15) - H_0°] = 1609.58$ cal$_{th}$ mol^{-1}. This difference was determined by using the heat capacity data in ref. *21*. The best value of the heat of vaporization as per Reaction 2 is $\Delta H_0° = 124.4 \pm 0.4$ kcal$_{th}$ mol^{-1}, disregarding unknown systematic errors, compares with the value $\Delta H_0° = 129.5 \pm 5$ kcal$_{th}$ mol^{-1}, previously reported (*9*).

Another enthalpy difference required in the cycle is that of Reaction 1 which is the heat of formation of NiO. The best value available for this quantity is that obtained in ref. *19* which is $\Delta Hf_0° = 56.67 \pm 0.13$ kcal$_{th}$ mol^{-1}. The mass-spectrometric data of ref. *3*, corrected by us for errors in the cross sections by multiplying the reported pressures of O_2 by a factor of 1.25, $[1.25\ P_1(O_2) = P_2(O_2)]$, gives a third-law value of $\Delta Hf_0° = 57.4 \pm 0.3$ kcal$_{th}$ mol^{-1}. The values of $\Delta H°$ for Equations 1, 2, 4, and 5 can now be added to obtain a value for the dissociation energy of NiO(g). The result is $D_0°[NiO(g)] = 92.7 \pm 0.9$ kcal$_{th}$ mol^{-1}. The error in $D°$ is determined from the rms of sums of the squares of the percentage errors of each of the quantities in the cycle. Previously reported values of $D_0°[NiO(g)]$ are 86.5 (*9*), 87.0 (*38*) kcal$_{th}$ mol^{-1}, and <4.2 eV (*13*) (96.6 kcal$_{th}$ mol^{-1}).

Evaluation of Heat of Dissociation of Ni_2

In the course of the work reported here, we required a value of the $D_0°[Ni_2(g)]$ to determine the ionicity of the NiO(g) molecule. A value of 53.3 kcal$_{th}$ mol^{-1} was reported by Kant (*17*); however, examination of Kant's data revealed several errors. For example, there was an error in determining the ratios of the expected isotopic abundance of the species Ni_2^{ij}, where i and j represent the various isotopes of nickel. This error does not a priori invalidate the reported ionic current ratios in the mass spectrometer; however, it does throw some doubt on the efficacy of the experimental method. A discussion of these errors is given in ref. *36*.

In contrast, the error in assigning an electronic configuration to the ground state of the $Ni_2(g)$ molecule and an error in the equation used to determine $D_0°[Ni_2(g)]$ does change the value of $D°$ significantly. An examination of the possible electronic configurations of Ni_2 by the method described by Herzberg (*12b*) leads one to the assumption that for a homonuclear diatomic molecule, such as Ni_2, the most probable ground state is $^1\Sigma$ which gives a degeneracy of one instead of an average of 2.45 as used by Kant (*17*).

There was also an error in the expression for the relation between the dissociation energy and pressure used by Kant (Equation 1 (*17*)]. The constant in Equation 1 should be 3.2771 instead of 2.8247. This equation was originally proposed by Drowart and Honig (*7*). Table VII gives the data used in obtaining our values of $D°$. After making corrections to Kant's data, a value of $D_0°[Ni_2(g)] = 61.7 \pm 0.6$ kcal$_{th}$ mol^{-1} is obtained disregarding unknown systematic errors instead of Kant's reported value 53.3 kcal$_{th}$ mol^{-1}.

Evaluation of Ionization Cross Sections

In the above discussion, we have noted that the absolute and relative ionization cross sections used by Grimley et al. (*9*) differed significantly from those obtained from presently available data. We examined the available information on cross sections and performed an analysis to determine the best available values. An extensive report on the available ionization cross sections is given by Kieffer and Dunn (*20*). Keeping in mind that the relative cross sections which are often used are those calculated by Oetvos and Stevenson (*32*) and that these in principle refer to the maximum value of the ionization cross section, we corrected the relative ionization cross sections (Table VIII), and we propose that these values are the best available data. A detailed description of the critical method used in arriving at these values is given in ref. *36*.

The following relation is commonly used to determine the ionization cross section at an electron energy other than that of the maximum (*10*).

$$\frac{\sigma(V)}{\sigma(V, m)} = \frac{V - (V, A)}{(V, m) - (V, A)} \qquad (21)$$

In the above expression, $\sigma(V, \text{cm}^2)$ is the cross section at the voltage V, (V, A) is the appearance potential of the ion in question, and (V, m) is the potential at which the ionization cross section is a maximum. This relation was used to obtain values of ionization cross sections in Table VIII at energies other than of the maximum cross section.

Summary

The best available value of the change in enthalpy of Reaction 5 was determined by statistically treating our experimental value in combination with other data in the literature. The literature values of the enthalpy changes of Reactions 2 and 3 have been corrected utilizing more recent spectroscopic data and ionization cross sections. The thermodynamic cycle depicted by Reactions 1-5 yielded a value of $D_0°(NiO) = 92.7$ kcal$_{th}$ mol^{-1} when closed.

Table VIII. Ionization Cross Sections

Species	Electron energy, eV	Cross section,[a] $\sigma \times 10^{+16}$/cm^2	Cross section rel, σ(O + S)[b,c]	Exptl cross section rel
H	57.5[c,e]	0.68[e] ± 0.02[a]	1	1
O	87.8[c,f]	1.56[f] ± 0.06[a]	3.29	2.29
O_2	123.0[c,d]	2.80[c] ± 0.11[a]	6.58	4.12
Ag	72[c,g]	4.63[g] ± 1.0[h]	34.8	6.83
Ag	50	4.48[g] ± 1.0[h]		
Ag	60	4.50[g] ± 1.0[h]		
Ni	60	4.10[i] ± 1.0[h]		
Ni	(70)[c,j]	4.19 ± 1.0[h]	24.4	

[a] Estimate of random error. [b] Ref. **32**. [c] Maximum. [d] Ref. **20** (p 18, Figure 17). The total ionization cross section was used for these calculations because the electron energy which is used in mass-spectrometric studies may vary from 10–70 eV, but it is often limited to 20 eV. Dissociation of O_2 can be neglected at this energy. In cases where the electron energy is greater than 20 eV, corrections in O_2 current should be made for the dissociation of O_2 (**20**, p 43). [e] Ref. **20** (p 11, Figure 3). [f] Ref. **20** (p 12, Figure 6), data of Rothe and Fite. [g] Ref. *5* (Figure 2). [h] Estimate of total error. [i] Combination of data (*4*, *5*, and *35*). [j] Estimated.

(1) $Ni(s) + \frac{1}{2}O_2(g) \rightarrow NiO(s)$

$$\Delta Hf_0° = -56.67 \pm 0.13 \text{ kcal}_{th} \text{ mol}^{-1}$$

(2) $NiO(s) \rightarrow NiO(g) \quad \Delta H_0° = 124.4 \pm 0.4$ kcal$_{th}$ mol^{-1}

(3) $NiO(g) \rightarrow Ni(g) + O(g)$

$$\Delta H_0° = 92.7 \pm 0.9 \text{ kcal}_{th} \text{ mol}^{-1}$$

(4) $O(g) \rightarrow \frac{1}{2}O_2(g)$

$$\Delta H_0° = -58.969 \pm 0.005 \text{ kcal}_{th} \text{ mol}^{-1}$$

(5) $Ni(g) \rightarrow Ni(s) \quad \Delta H_0° = -101.5 \pm 0.6$ kcal$_{th}$ mol^{-1}

"Best" vapor-pressure equations based on third-law values of the parameters were determined for both solid and liquid nickel. The liquid nickel vapor-pressure equation in the literature required a small correction.

$\ln P(\text{Ni, s, atm}) = 16.87 \pm 0.35 - (50600 \pm 500)\ (T^{-1})$ between 1250 and 1710K

$\ln P(\text{Ni, l, atm}) = 15.35 \pm 0.05 - (47775 \pm 210)\ (T^{-1})$ between 1816 and 1895K

Corrected estimated value of the heat of dissociation: $D_0°[Ni_2(g)] = 61.7 \pm 0.6$ kcal$_{th}$ mol^{-1}.

The best value of the maximum (m) ionization cross section of various species required in mass-spectrometric determinations of pressures are as follows at the voltages noted.

$$\sigma(H, 57.5/V, m) = 0.68 \pm 0.02 \times 10^{-16} \text{ cm}^2$$

$$\sigma(O, 87.8/V, m) = 1.56 \pm 0.06 \times 10^{-16} \text{ cm}^2$$

$$\sigma(O_2, 123/V, m) = 2.80 \pm 0.11 \times 10^{-16} \text{ cm}^2$$

$$\sigma(Ag, 72/V, m) = 4.63 \pm 1.0 \times 10^{-16} \text{ cm}^2$$

$$\sigma(Ni, 70/V, m) = 4.19 \pm 1.0 \times 10^{-16} \text{ cm}^2$$

Literature Cited

(1) Branscomb, L. M., Burch, D. S., Smith, S. J., Geltman, S., *Phys. Rev.*, **111**, 504 (1958).
(2) Brewer, L., Chandraschrakaraish, "Free Energy Functions of Gaseous Monoxides," University of California, Lawrence Radiation Laboratory, Report No. UCRL-8713 (Rev), June 1960.
(3) Bryce, G., *J. Chem. Soc.*, **1936**, p 1517.
(4) Cooper, Jr., J. L., Pressley, Jr., G. A., Stafford, F. E., *J. Chem. Phys.*, **44**, 3496 (1966).
(5) Crawford, C. K., "Electron Impact Ionization Cross Sections," Air Force Materials Lab, Report AFML-TR-67-376, AD826983, Dec. 1967.
(6) Deming, W. E., "Statistical Adjustment of Data," pp 168–71, Dover, 1964.
(7) Drowart, J., Honig, R. E., *J. Phys. Chem.*, **61**, 980 (1957).
(8) Fisher, R. A., Yates, F., "Statistical Tables for Biological, Agricultural and Medical Research," 4th ed., Hafner, New York, N.Y., 1953.
(9) Grimley, R. T., Burns, R. P., Inghram, M. G., *J. Chem. Phys.*, **35**, 551 (1961).
(10) Grimley, R. T., in "Characterization of High Temperature Vapors," J. L. Margrave, Ed., p 223, Wiley, New York, N.Y., 1967.
(11) Herzberg, G., "Molecular Spectra and Molecular Structure; II. Infrared and Raman Spectra of Polyatomic Molecules," pp 501–30, Van Nostrand, New York, N.Y., 1945.
(12) Herzberg, G., "Spectra of Diatomic Molecules," 2nd ed., (a) p 372, (b) pp 371–77, Van Nostrand, New York, N.Y., 1950.
(13) Huldt, L., Lagerquest, A., *Z. Naturforsch.*, **9**, 358 (1954).
(14) Hultgren, R. R., Anderson, P. D., Kelley, K. K., "Selected Values of the Thermodynamic Properties of Metals and Alloys," 1966, Supplement, Wiley, New York, N.Y., 1963.
(15) JANAF Thermochemical Tables, Nat. Ref. Data System, Nat. Bur. Stand., Supt. of Documents, GPO, Washington, D.C. 20402.
(16) Johnston, H. L., Marshall, A. L., *J. Amer. Chem. Soc.*, **62**, 1382 (1940).

(17) Kant, J. A., *J. Chem. Phys.*, **41**, 1872 (1964).
(18) Kelley, K. K., "Contributions to the Data on Theoretical Metallurgy; XIII. High Temperature Heat Content, Heat Capacity, and Entropy Data for the Elements and Inorganic Compounds," Bulletin 584, Bureau of Mines, Washington, D.C., 1960.
(19) Kellogg, H. H., *J. Chem. Eng. Data*, **14**, 41 (1969).
(20) Kieffer, L. J., Dunn, G. W., *Rev. Mod. Phys.*, **38**, 1 (1966).
(21) King, E. G., *J. Amer. Chem. Soc.*, **79**, 2399 (1957).
(22) Langmuir, I., Jones, H. A., MacKay, G. M. J., *Phys. Rev.*, **30**, 26 (1927).
(23) Langmuir, I., "The Collected Works of Irving Langmuir," Vol 9, p 3, Pergamon, New York, N.Y., 1916.
(24) Mallet, L., Rosen, B., *Bull. Soc. Roy. Sci., Liege*, **14**, 382 (1945).
(25) Mandel, John, "The Statistical Analysis of Experimental Data," Chap. 5, Interscience, New York, N.Y., 1964.
(26) Mandel, John, Paule, R. C., *Anal. Chem.*, **42**, 1194 (1970).
(27) Moore, C. E., *Nat. Bur. Stand.*, Circular No. 467, 1959.
(28) Morris, J. P., Zellars, G. R., Payne, S. L., Kipp, R. L., "Vapor Pressure of Liquid Iron and Liquid Nickel," U.S. Bureau of Mines, Report No. 5364, 1957.
(29) Nesmeyanov, An. N., Tik-Mang, Teh, *Dokl. Akad. Nauk SSSR*, **116**, 230 (1957).
(30) Nesmeyanov, An. N., Tik-Mang, Teh, *Izv. Akad. Nauk SSR, Otd. Tekh. Nauk* (1), 75 (1960).
(31) Nesmeyanov, An. N., "Vapor Pressure of the Elements," J. I. Carasso, Transl., p 396, InfoSearch, London, England, 1963.
(32) Oetvos, J. W., Stevenson, D. P., *J. Amer. Chem. Soc.*, **78**, 546 (1956).
(33) Paule, R. C., Mandel, John, "Analysis of Interlaboratory Measurements on the Vapor Pressures of Cadmium and Silver," NBS Spec. Publ. 260-21, Nat. Bur. Stand., Washington, D.C., 1971.
(34) Pauling, L., "Nature of the Chemical Bond," (a) p 62, (b) p 256, Cornell Univ. Press, Ithaca, N.Y., 1960.
(35) Rovner, L. H., Norman, J. H., *J. Chem. Phys.*, **52**, 2496 (1970).
(36) Rutner, Emile, Haury, G. L., "The Vapor Pressure and Heats of Vaporization of Nickel," Tech. Report AFML-TR-72-217, Air Force Materials Lab, Wright-Patterson AFB, Ohio, 1972.
(37) Stull, D. R., Sinke, G. C., "Thermodynamic Properties of the Elements," American Chemical Society, Washington, D.C., 1956.
(38) Trivedi, Hrishikesha, *Proc. Nat. Acad. Sci., India*, *4*, 27 (1935).
(39) Wang, K. L., Brody, M. D., Crawford, C. K., Air Force Materials Lab, Report AFML-TR-69-5, Jan. 1969.
(40) Weast, R. C., Ed., "Handbook of Chemistry and Physics," 47th ed., Chemical Rubber Co., Cleveland, Ohio, 1966.
(41) Wickes, C. E., Block, F. E., "Thermodynamic Properties of 65 Elements, Their Oxides, Halides, Carbides, and Nitrides," Bulletin 605, Bureau of Mines, Washington, D.C., 1963.
(42) Yamashito, Jiro, Masa, Kojima, *J. Phys. Soc., Japan*, **7** (3), 261 (1952).

Received for review May 14, 1973. Accepted September 27, 1973.

Liquid and Vapor Densities of Aluminum Bromide

David S. Olson, Fred C. Kibler, Jr., David W. Seegmiller, Armand A. Fannin, Jr., and Lowell A. King[1]
Frank J. Seiler Research Laboratory (Air Force Systems Command) and Department of Chemistry,
United States Air Force Academy, Colo. 80840

The orthobaric liquid and vapor densities of aluminum bromide were measured from 92° to 319°C. The method simultaneously yielded the liquid and vapor densities for each (arbitrary) experimental temperature. The experimental precision was ± 0.0025 g/cm^3, which corresponds to 0.1% of the liquid densities, and ranged from 6 to 100% of the vapor densities over the temperature range covered. A single empirical equation was derived which was symmetrical about the rectilinear diameter and which represented both liquid and vapor densities.

As part of a program for the investigation of certain low-melting, molten salt electrolytes for high energy density batteries, we needed to know the densities of aluminum bromide liquid and vapor. Many of the physical properties of aluminum bromide have been collected in a review by Boston (*2*). Biltz and Voight (*1*) earlier had measured a few liquid densities from 100° to 265°C, Zhuravlev (*10*) measured liquid densities from 170° to 450°C, and Johnson et al. (*4*) determined liquid and vapor densities in the temperature ranges 101–490°C and 270–488°C, respectively. We were interested primarily in the densities near the melting point, which was reported to be 97.5°C (*9*).

Experimental

Aluminum bromide was synthesized by dropping Mallinckrodt analytical reagent Br_2 onto J. T. Baker purified granular aluminum contained in a flask in which a slight positive pressure of dry Ar was maintained. After the synthesis was complete, $AlBr_3$ was distilled out of the reaction flask into a clean container. The distillate crystals were transferred (inside a glove box) to an ampul which was then evacuated and sealed, and a further purification carried out by growing crystals from the vapor phase. This latter process was done in a manner analogous to the method we formerly used for $AlCl_3$ (*8*).

Orthobaric liquid and vapor densities were simultaneously determined from 363 measurements made substantially as we reported earlier for our work with aluminum chloride (*5*, *7*). Thirteen sealed borosilicate glass dilatometric tubes were used. These each consisted of two bulbs connected by a calibrated, graduated capillary. The tubes were held vertically, such that liquid $AlBr_3$ filled the lower bulb and extended into the graduated capillary. The upper part of the capillary and the upper bulb contained $AlBr_3$ vapor.

The filled bulbs were immersed in a molten salt bath, and at each different temperature the distance from the bottom of the $AlBr_3$ meniscus to an arrow etched on the capillary was measured with the aid of a cathetometer. From this measurement and the tube calibration data, the liquid volume was calculated.

The dilatometric tubes were identical in general size and design to those described in ref. 5. They were calibrated in the same manner employed for tubes *A*, *B*, *C*, and *D* of that report. Meniscus corrections and thermal expansion corrections, the molten salt bath, and the bath temperature control were also as described therin. Bath temperature was determined by measuring the resistance of a 4-wire platinum resistance element (Electric Thermometers Trinity, Inc., Bridgeport, Conn. 06604) (100 Ω nominal) calibrated against the platinum Air Force Reference Standard Thermometer which we used earlier (*7*).

Tube calibration data are given in Tables I and II. The distances from $AlBr_3$ menisci to the arrows etched on the capillaries are shown in Table III. Without using unduly large capillaries (or small bulbs), it was not possible for a single tube to span the entire temperature range of interest. We divided the 13 tubes into five groups covering

---

[1] To whom correspondence should be addressed.