namic ionization constant of monoethanolammonium hydroxide has been calculated and found to be 3.19×10^{-5} at 25°.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE GENERAL ELECTRIC COMPANY]

Vapor Pressures of Nickel and of Nickel Oxide

BY H. L. JOHNSTON* AND A. L. MARSHALL

Vapor pressures of copper and of iron, determined by measuring the rates of evaporation from metal rings heated inductively in a vacuum, were recently published from this Laboratory.[1] We have completed a similar investigation with nickel between the temperatures of 1300 and 1600°K., and have also determined vapor pressures of nickel oxide, by measuring rates of nickel and of oxygen loss from nickel rings coated with a thin film of the oxide. From these data, and thermodynamic and quantum-statistical data on both the solid and gaseous forms of nickel and of nickel oxide, we have computed their heats of sublimation and have derived vapor pressure formulas.

Vapor pressures, p, are computed from the measured rates of evaporation, m, by use of the relationship[1,2]

$$\log p + \log \alpha = \log m - {}^1/_2 \log M + {}^1/_2 \log T - 1.647 \quad (1)$$

where p is in atmospheres; m is in grams per square centimeter per second; M is the molecular weight in the vapor phase; T the absolute temperature; and α, termed the *accommodation coefficient*, is a measure of the efficiency with which molecules that strike the equilibrium surface from the vapor phase are condensed. The accommodation coefficient is unity if condensation results at every collision.

As with copper and with iron, the results with nickel establish this coefficient as unity and support the general validity of the Langmuir method in its application to metals. Vapor pressures, and the accommodation coefficient, could not be determined for the oxide with the same accuracy as for the metal, but the accommodation coefficient appears to be unity within the limits of experimental error.

Nickel

Experimental.—Apparatus and procedure were described previously.[1] Except as noted below the same description applies here.

The nickel used, in all but one of the runs, was electrolytic in origin and had been vacuum melted in an alundum crucible. Spectrographic analysis indicated the absence of any impurity, in significant amount, other than cobalt. The latter was present to the extent of 0.64% in the original specimen and, within limits of a colorimetric method employed for the analysis, this percentage remained unchanged in the evaporated film.[3] The results obtained in a single (subsequent) run[4] with a ring turned from pure carbonyl nickel[5] were undistinguishable from those obtained with the electrolytic nickel.

Dimensions of the nickel ring turned from the vacuum ingot were: outer diameter, 2.23 cm.; inner diameter, 1.13 cm.; thickness, 0.63 cm.; total surface, 12.46 sq. cm. Correction for condensation of atoms which strike the inner surface of the ring reduces the effective surface area to 11.74 sq. cm.

Evaporation losses were determined by weighing the approximate 16 g. ring on a sensitive balance. Weighings were reproducible to within 0.02 milligram.

Temperatures were determined by setting the filament of the optical pyrometer on two holes, 1.2 mm. in diameter, drilled vertically into the face of the specimen to a depth of about four millimeters. Measurements on a specimen drilled with holes of 0.6 mm., 1.2 mm. and 1.8 mm. diameter proved that the emissivity from the 1.2 mm. hole was indistinguishable from that from the 0.6 mm. hole to the highest temperature to which measurements were carried, 1600°K., and was therefore the equivalent of black body radiation. On the other hand, the emissivity from the 1.8 mm. hole was definitely less than black body at 1100° and yielded brightness temperatures more than twenty degrees in error at 1600°.

Temperatures determined as described above were normally reproducible within limits of approximately three degrees (each determination the average of five to ten successive observations). This corresponds to limits of approximately 10% on individual vapor pressure determinations. Temperatures were taken continuously during

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[1] Marshall, Dornte and Norton, THIS JOURNAL, **59**, 1161 (1937).

[2] Langmuir, *Phys. Rev.*, **2**, 329 (1913).

[3] The influence of this amount of cobalt on the measurements of the evaporation of nickel must lie well within the accuracy of the latter. The observation that the composition of the evaporated metal is identical with that of the original specimen within limits of the analytical error indicates that vapor pressures of cobalt and of nickel are nearly equal, which is in agreement with the data of Ruff and Bormann (*Z. anorg. Chem.*, **88**, 386, 397 (1914)) on liquid nickel and cobalt.

[4] Run M in the tables. This run was made by Dr. F. J. Norton and Dr. R. W. Dornte.

[5] The metal for this ring was furnished through the courtesy of the International Nickel Co. Its composition was stated to be: 99.89% nickel, 0.048% iron, 0.035% carbon, 0.014% copper and 0.008% sulfur.

TABLE I

VAPOR PRESSURES OF NICKEL

Run	Temp., °K.	Time, seconds	Effective time, seconds	Wt. loss, g.	m g./sq. cm./sec.	p, atm.
4	1307	67,680	68,942	0.00457	5.65×10^{-9}	6.00×10^{-10}
7	1308	2,580	1,948	(.00012)[7]	(5.3×10^{-9})	(5.6×10^{-10})
6	1387	19,620	19,600	.01196	5.20×10^{-8}	5.70×10^{-9}
10	1397	20,640	19,632	.01517	6.58×10^{-8}	7.24×10^{-9}
11	1397	(11,100)[8]	(11,272)	.00980	(7.41×10^{-8})	(8.16×10^{-9})
5	1415	11,040	9,856	.01142	9.87×10^{-8}	1.09×10^{-8}
2	1465	3,480	3,325	.0129	3.30×10^{-7}	3.72×10^{-8}
9	1466	10,740	10,152	.04570	3.83×10^{-7}	4.33×10^{-8}
1	1507	1,980	1,872	.0191	8.69×10^{-7}	9.92×10^{-8}
8	1576	1,680	1,882	.08539	3.87×10^{-6}	4.52×10^{-7}
3	1578	1,550	1,481	.06774	3.89×10^{-6}	4.55×10^{-7}
M	1583	2,362	1,972	.0808	3.98×10^{-6}	4.63×10^{-7}

short runs and at frequent intervals during longer runs. Corrections were applied for evaporation losses during a preliminary period of degassing the nickel and during the period that the sample was coming up to temperature. Corrections were also made for small temperature fluctuations that sometimes resulted from variations in operating conditions during the period of the run. It was found convenient to make these corrections graphically by plotting relative evaporation rates (obtained as a function of the temperature) against time and to apply them to yield an "effective" length of run at constant rate of evaporation. The magnitudes of these corrections may be judged by comparison of the third and fourth columns of Table I.

The pyrometer used in this work was the one previously employed by Marshall, Dornte and Norton,[1] and calibrated by them against a standard tungsten ribbon filament lamp (designated as Standard Lamp W 91) supplied and calibrated by Forsythe.[6] The pyrometer calibration has been rechecked by Dr. R. W. Dornte subsequent to the work reported in this paper, and found not to deviate from the earlier calibration.

Window corrections which normally amounted to about 12 degrees, were determined by calibrations *in situ*.

Data.—The experimental results are recorded in Table I. All of our runs are included although 7 and 11 are entitled to less weight than the others. Runs 1 to 7 inclusive were made with a preliminary 600–700° bakeout in vacuum. In runs 8 to 11 hydrogen was present during the bakeout. There was no significant difference in results.

Thermodynamic Treatment.—The reliability of vapor pressure data is best confirmed by establishing the constancy of ΔH_0° in the thermodynamic relationship

$$R \ln p \text{ (atmospheres)} = \left(\frac{F^\circ - H^\circ}{T}\right)_{\text{condensate}} - \left(\frac{F^\circ - H_0^\circ}{T}\right)_{\text{vapor}} - \frac{\Delta H_0^\circ}{T} \quad (2)$$

applied to the individual data. Here $F^\circ - H_0^\circ/T$ for a solid is calculable from its heat capacity by the equation

$$\left(\frac{F^\circ - H_0^\circ}{T}\right)_{\text{solid}} = \frac{1}{T}\int_0^T C_p \mathrm{d}T - \int_0^T C_p \mathrm{d} \ln T \quad (3)$$

and $(F^\circ - H_0^\circ/T)_{\text{vapor}}$ can be evaluated accurately by statistical methods which depend partly on information gained from the spectrum.[9] ΔH_0° has the significance of the heat of sublimation to ideal gas at the absolute zero.

Kelley[10] has reviewed the experimental data on solid nickel published prior to 1934, and has computed and tabulated the free energy function on the basis of these data. More recent work[11] indicates that the heat capacity curve in the high temperature region should run somewhat under the values adopted by Kelley. We have accordingly recalculated the thermodynamic functions for solid nickel to conform with the newer data. The results, which differ from Kelley's tables by amounts sufficient to make a difference of about 0.3 of a unit in the free energy function at 1500°, are entered in Table II, together with the free energy function for nickel vapor computed by Overstreet[12] and quoted by Kelley.[10] The last column is the change in the standard free energy function, in the evaporation of nickel.

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[6] Forsythe, *J. Optical Soc. Am.*, **4**, 305 (1920).

[7] This figure is the smoothed average of the weight determination (0.00014 g.) and of a colorimetric determination of nickel in a nitric acid solution of the deposit formed on the walls of the cell (0.000104 g.). Colorimetric determinations on deposits from other runs differed from the more accurate weight determinations by amounts which were generally under 5% but doubled this percentage in one or two instances.

[8] There is an uncertainty of approximately eleven minutes in the duration of Run 11 due to the fact that the power went off unexpectedly during a period when the apparatus was not under continuous observation. This is equivalent to a 6% uncertainty in evaporation rate and in pressure.

[9] W. F. Giauque, THIS JOURNAL, **52**, 4808 (1930).

[10] K. K. Kelley, *Bureau of Mines Bulletin*, **350**, 34 (1932); *ibid.*, **371**, 36 (1934); *ibid.*, **383**, 73 (1935).

[11] Grew, *Proc. Roy. Soc.* (London), **A145**, 509 (1934); Ahrens, *Ann. Physik*, **21**, 169 (1934); Clusius and Goldmann, *Z. physik. Chem.*, **B31**, 256 (1936); Rosenblum and Jaeger, *Proc. Acad. Sci. Amsterdam*, **39**, 366 (1936); Ewert, *ibid.*, **39**, 833 (1936); Bronson, Hewson and Wilson, *Can. J. Research*, **14A**, 181, 194 (1936); Steinwehr and Schulz, *Phys. Z.*, **37**, 753 (1936); Moser, *ibid.*, **37**, 737 (1936).

[12] R. Overstreet, Master's Thesis, University of California, 1930.

TABLE II

THERMODYNAMIC FUNCTIONS OF NICKEL AND CHANGE OF THE STANDARD FREE ENERGY FUNCTION IN THE EVAPORATION

T, °K.	$H^\circ - H^\circ$	$(H^\circ - H^\circ_0)/T$	S°	$\left(\frac{F^\circ - H^\circ_0}{T}\right)_{\text{solid}}$	$\left(\frac{F - H^\circ_0}{T}\right)_{\text{vapor}}$	$\Delta\left(\frac{F - H^\circ_0}{T}\right)_{\text{evap.}}$
298.1	1142	3.83	7.02	− 3.19	−38.058	−34.87
400	1800	4.50	8.92	− 4.42	−39.672	−35.25
500	2507	5.01	10.46	− 5.44	−40.908	−35.47
600	3286	5.48	11.88	− 6.40	−41.929	−35.53
700	4068	5.81	13.09	− 7.28	−42.796	−35.52
800	4801	6.00	14.07	− 8.07	−43.557	−35.49
900	5538	6.15	14.93	− 8.78	−44.231	−35.45
1000	6283	6.28	15.72	− 9.44	−44.831	−35.39
1100	7038	6.40	16.44	−10.04	−45.382	−35.34
1200	7802	6.50	17.10	−10.60	−45.885	−35.28
1300	8574	6.60	17.72	−11.13	−46.348	−35.22
1400	9354	6.68	18.30	−11.62	−46.777	−35.16
1500	10141	6.76	18.84	−12.08	−47.174	−35.10
1600	10936	6.84	19.35	−12.51	−47.548	−35.04
1700	11739	6.91	19.84	−12.93	−47.901	−34.97

Our values are based principally on the data of Keesom and Clark[13] for temperatures below 10°K.; on those of Clusius and Goldmann[11] for the interval 10 to 26°; those of Eucken and Werth[14] and of Rodebush and Michalek[15] for the interval 25 to 200° and on the recent careful work of Moser[11] for the interval 300 to 1000°K. Above 1000°K. we have extrapolated the curve of Moser by continuing it parallel to that of Ewert.[11] There may be an uncertainty of 100 calories in the enthalpy at 1600° in this extrapolation, but this will be almost fully compensated in the entropy term. The work of Moser on pure carbonyl nickel, with a carefully controlled adiabatic calorimeter, appears to justify this weighting to the exclusion of earlier data. The enthalpy values secured from Moser's data are in good agreement with the total heats between room temperature and about 800°K., determined by Bronson, Hewson and Wilson who estimate their limits of error at 0.2 of 1%. The entropy of the magnetic transformation was obtained by dividing Moser's heat input for the interval 600 to 673° by 641°, the "center of gravity" of this input, determined from the C_p *vs.* log T plot.

TABLE III

ΔH°_0 FOR THE EVAPORATION OF SOLID NICKEL

Run	T, °K.	4.575 $\log_{10} p$	$\Delta\left(\frac{F^\circ - H^\circ}{T}\right)_{\text{evap.}}$	ΔH°_0
4	1307	−42.19	35.21	101,162
7	1308	(−42.31)	35.21	(101,403)
6	1387	−37.72	35.17	101,098
10	1397	−37.24	35.16	101,143
11	1397	(−37.01)	35.16	(100,815)
5	1415	−36.42	35.15	101,272
2	1465	−33.99	35.12	101,246
9	1466	−33.69	35.12	100,875
1	1507	−32.04	35.10	101,172
8	1576	−29.03	35.05	100,990
3	1578	−29.02	35.05	101,102
M	1583	−28.98	35.05	101,359

Average ΔH°_0 (Runs 7 and 11 not included), 101,141 ± 150 cal.

Table III gives the values of the sublimation heat at 0°K., obtained by combination of the data of Table II with the experimental vapor pressures recorded in Table I.

Substitution of the average ΔH°_0 into equation (2), with a linear expansion of $\Delta(F^\circ - H_0/T)$ as a function of T (Table II), leads to the vapor pressure equation

$$\log p \text{ (atmospheres)} = -\frac{22{,}107}{T} - 1.31 \times 10^{-4}T + 7.869 \quad (4)$$

which we believe accurate to within 5% of the pressure. The fit with our experimental data is shown graphically in Fig. 1. The curve in this graph is constructed from equation (4), and the radii of the circles drawn to correspond to the uncertainty in the individual measurements (±3° in all runs except Nos. 7 and 11).

The Accommodation Coefficient.—The good agreement of ΔH°_0 among runs, and the absence of any temperature trend, establish the accommodation coefficient as unity within sensible limits of error. This depends on the fact that, for α other than unity, the entries in the third column of Table III would be in error by the amount 4.575 log α, and those in the fifth column by the

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[13] W. H. Keesom and C. W. Clark, *Physica*, **2**, 513 (1935).

[14] A. Eucken and H. Werth, *Z. anorg. Chem.*, **188**, 152 (1930).

[15] W. H. Rodebush and J. C. Michalek, THIS JOURNAL, **47**, 2117 (1925).

amounts 4.575 $T \log \alpha$. The values of the *supposed* ΔH_0° would thus vary with the temperature at a rate proportional to the magnitude of α (except in the fortuitous case that $\log \alpha$ vary in exact inverse proportion to T). The absence of any sensible variation in the ΔH_0°'s computed from the nickel data thus makes it reasonably certain that the accommodation coefficient for nickel is unity. The data would not preclude an α intermediate between 0.75 and 1.00, however.[16]

This conclusion receives qualitative confirmation from: (1) the absence of condensation in the re-entrant portions of the quartz cell[17]; and (2) the observation that, within limits of error, the loss in weight per unit time is no different for a nickel cylinder perforated with many deep, narrow drill holes than for a non-perforated cylinder of equal external dimensions.[18]

Comparison with other Investigators.—Rates of evaporation from nickel surfaces have been reported previously by Jones, Langmuir and Mackay[19] and by Bryce.[20] These data are entered in Table IV and Fig. 1, and ΔH_0°'s likewise computed.

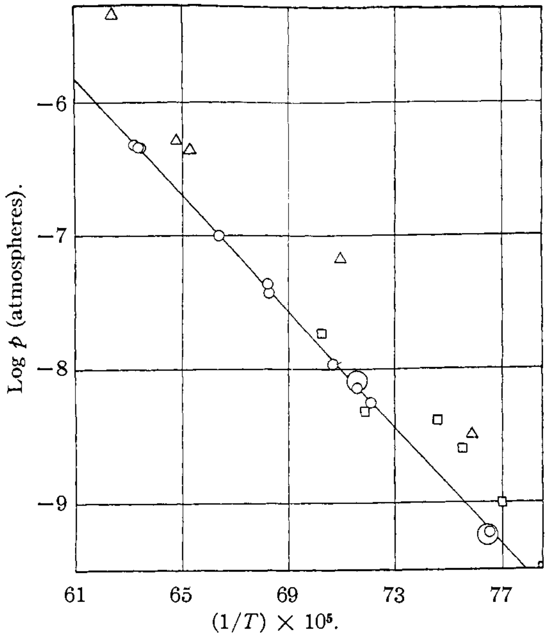

Fig. 1.—Vapor pressures of nickel: ○, this research; △, Jones, Langmuir and Mackay; □, Bryce. The dimensions of the circles, representing this research, are drawn in scale to represent error limits. The curve is constructed from equation (4).

TABLE IV

VAPOR PRESSURES OF NICKEL REPORTED BY OTHER OBSERVERS

T, °K.	p (atm.)	ΔH_0°	Observer
1252	1.29×10^{-10}	100,460	Bryce
1273	3.22×10^{-10}	99,808	Bryce
1299	9.88×10^{-10}	98,932	Bryce
1318	3.20×10^{-9}	97,276	J., L. & M
1324	1.38×10^{-9}	99,922	Bryce
1341	1.45×10^{-9}	100,119	Bryce
1391	4.85×10^{-9}	101,432	Bryce
1409	6.67×10^{-8}	95,375	J., L. & M.
1423	1.84×10^{-8}	99,952	Bryce
1532	4.34×10^{-7}	97,827	J., L. & M.
1544	5.06×10^{-7}	98,107	J., L. & M.
1602	4.38×10^{-6}	97,925	J., L. & M.

Both Langmuir and co-workers and Bryce measured evaporation losses from nickel filaments. The ring evaporation method possesses the advantage of being free from the following sources of error, which are difficult to avoid in filament evaporation: the considerable variation in evaporation rate in the course of each run due to decrease in the dimensions of the filament; the effect of superheating at thin spots in the filament; the difficulty of obtaining good pyrometer settings on a thin wire and of properly correcting for temperature gradients along the wire and the necessity of making corrections for surface emissivity.[21]

Nickel Oxide

Experimental.—The rings used to determine evaporation rates of nickel oxide were of approximately the same

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[16] If one out of every four atoms fails to condense on the *hot* surface at equilibrium (an accommodation coefficient of 0.75) there would result an apparent increase in ΔH_0° of 180 calories, between 1300° and 1600°. This is just under the precision of our measurements (±300 calories on individual points from an estimated limit of 3° in temperature). Actually, our deviations from the mean ΔH_0° lie within 150 calories with two exceptions.

[17] This relates directly to the accommodation coefficient on a *cold* surface while the calculation of vapor pressures from evaporation rates requires a knowledge of the accommodation coefficient on the *hot* equilibrium surface. We may ordinarily expect the accommodation coefficient to be unity on both hot and cold surfaces if unity on either but this is not a necessary consequence and is apparently not true in the case of graphite (which we expect to discuss in a subsequent communication).

[18] This is evidence that atoms evaporated from the walls of the drill holes are recondensed before they reach the surface. The data obtained with the nickel cylinders will be included in a subsequent paper on the evaporation of graphite.

[19] H. A. Jones, I. Langmuir, and G. M. J. Mackay, *Phys. Rev.*, **30**, 20 (1927).

[20] Bryce, *J. Chem. Soc.*, 1517 (1936). Dr. Bryce kindly communicated the numerical values of the data which he shows graphically in his paper, in correspondence with Dr. H. A. Liebhafsky of this Laboratory, and has consented to their use. The pressures attributed by us to Bryce, in our Table IV, and the corresponding values of ΔH_0°, were computed by us from Bryce's evaporation rates, with the aid of our equations (1) and (2).

[21] In conjunction with our own work we obtained a value of 0.41 for the emissivity of nickel at $\lambda = 0.665\ \mu$. This is slightly higher than the value employed by Jones, Langmuir and Mackay, but of the wrong sign and wrong magnitude to account for the approximately 50° discrepancy between their data and ours. Our own temperature scale in no wise depends on the value adopted for the emissivity of nickel since we obtained the equivalent of "black body" radiation.

dimensions as the one employed with nickel and were corrected in the same manner for condensation on the inner surface of the ring. Results obtained with rings turned from electrolytic nickel (0.64% cobalt) were indistinguishable from those obtained with a ring of carbonyl nickel.[5]

The rings were oxide coated prior to each run by oxidation in air for several minutes at about 900° and were partially degassed prior to evaporation by a preliminary bakeout in vacuum at about 400°. Uniform, adhering films of olive-green oxide were produced. Approximate calculations indicate that the film thicknesses varied from 10,000 to about 50,000 NiO layers. Lengths of runs were ordinarily chosen so that only 4 or 5% of the oxide coating was evaporated. One run (1566°K.) in which 35% of the oxide was evaporated yielded data in good agreement with the lesser removals of film.

The measurements were complicated by the fact that evaporation losses were made up in large part of pure nickel which escaped through the film. It was thus necessary to distinguish between total losses in weight and the weight loss of oxygen. The latter was obtained, by difference, through determination of the residual oxygen which remained on the ring. This determination was made by reducing the ring in an atmosphere of hydrogen at 800°. The reduction was repeated, for ten or twenty minute reduction periods, until the ring came to constant weight. This result was usually attained (within an accuracy of 0.01 or 0.02 mg.) with two reductions. The final weighing was corrected (a correction of 0.08 mg.)[22] for hydrogen dissolved in the nickel at 800°.

Temperatures were determined by pyrometer settings on 1.2-mm. holes drilled into the surface of the specimen.[23] Corrections for fluctuations in temperature and for preliminary heating periods were applied in the manner described for nickel.

No deposit was formed in the re-entrant portions of the cell. On the basis of this observation the accommodation coefficient was taken to be unity.

Data.—Data from a typical run are shown in Table V. Summaries from all of the runs are entered in Table VI.

TABLE V

DATA FROM RUN 4

Temperature, 1511°K. Effective time, 609 seconds

Initial wt. before oxidation, g.	15.46038
Wt. after oxidation, g.	15.46955
Wt. after evaporation, g.	15.46490
Wt. after H_2 reduction (corrected for dissolved hydrogen), g.	15.45613
By difference:	
Oxygen initially added, g.	0.00917
Evaporation loss (NiO + Ni), g.	.00465
Residual oxygen, g.	.00877
Oxygen evaporated (as NiO), g.	.00040
NiO evaporated, g.	.00187
Free nickel evaporated, g.	.00278
m (g./sq. cm./sec.) for NiO	2.62×10^{-7}
p (atm.)	2.66×10^{-8}

Thermodynamic Treatment.—The integral $\int_{296}^{T} C_p \mathrm{d}T$, for solid nickel oxide, has been measured by Kapustinsky and Novoseltsev[24] for various upper limits of the integral to 1396°K. They employed a high temperature calorimeter of new design.[25] Heat capacities between 68° and 298°K. have been measured with a vacuum calorimeter, by Seltz, DeWitt and McDonald,[26] who extrapolate their data to 0°K. by means of a combination of Debye and Einstein terms in accordance with the formula

$$C_p = D\left(\frac{404}{T}\right) + E\left(\frac{620}{T}\right) \qquad (5)$$[27]

They further find that their own data at 298° and the integrals $\int_{298}^{T} C_p \mathrm{d}T$ determined by Kapustinsky and Novoseltsev can be represented by the equation

$$C_p = 13.69 + 0.83 \times 10^{-3}T - 2.915 \times 10^{5}T^{-2} \qquad (6)$$

up to the highest limits of Kapustinsky's measurements (1396°K.). This represents an improvement over the equation published by Kapustinsky and Novoseltsev,[24] which fails to reproduce the heat capacity at low temperatures. The fact that the data can be so represented excludes the possibility of a transition below 1400°.

From the values[27] for $(H^{\circ}_{298.1} - H^{\circ}_{0})$ and for $S^{\circ}_{298.1}$ obtained from Seltz' data and from the integration of equation (6) between 298.1 and T we obtain, for the free energy function of solid nickel oxide, the relationship (*cf.* eq. 3)

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[22] This correction was determined experimentally by collecting, and measuring, the gas liberated from the ring of electrolytic nickel subsequent to one of the 800° reductions. To accomplish this the bare nickel ring was sealed into the quartz apparatus[2] and heated by means of high frequency to approximately 1000°. By means of a mercury diffusion pump the evolving hydrogen was pumped into a separate vessel of known volume and the final pressure was determined on a McLeod gage.

As the correction was not large, and care was taken always to reproduce the approximate 800° temperature and other experimental conditions under which reduction was brought about, it was considered justifiable to apply this same correction in all of the runs.

[23] The holes were clearly visible at temperatures above about 900°. We obtained an average value of 0.86 (for $\lambda = 0.665\ \mu$) for the emissivity of the oxide coated surface. This value is higher than that we have obtained for a specimen of graphite (0.53) and is a reasonable value. Consequently we may conclude that no significant temperature gradient exists between the oxide film and the metal.

[24] Kapustinsky and Novoseltsev, *J. Phys. Chem.* (U. S. S. R.), **11**, 61 (1938).

[25] Kapustinsky and Veselovsky, *ibid.*, **11**, 68 (1938).

[26] Seltz, DeWitt and McDonald, THIS JOURNAL, **62**, 88 (1940).

[27] The extrapolation below 68° contributes only 33 calories to $(H - H_0)$ and 0.65 E. U. to the entropy. We obtain $H^{\circ}_{298.1} - H^{\circ}_{0} =$ 1630 calories by graphical integration of Seltz's data, which was kindly furnished us in advance of its publication. Dr. Seltz (personal communication) informs us of an error in the published value of the entropy. The correct value is $S_{298.1^{\circ}} = 9.22$ E. U. We have used this corrected value in the subsequent calculations.

TABLE VI

VAPOR PRESSURES OF NICKEL OXIDE

Run	T, °K.	Effective time, sec.	Initial O_2, g.	Evap. loss, total g.	Residual O_2, g.	NiO evap., g.	Pressure, atm.
6	1438	6930	0.01424	0.01732	0.01381	0.00200	2.43×10^{-9}
5	1441	7001	.00759	.01160	.00722	.00173	2.09×10^{-9}
7	1495	2286	.01840	.01803	.01770	.00327	1.23×10^{-8}
4	1511	609	.00917	.00465	.00877	.00187	2.66×10^{-8}
Run 3 was lost through an accident							
2	1529	1340	.00921	.01139	.00837	.00392	2.72×10^{-8}
1	1566	759	.0044	.01893	.00289	.0070	8.51×10^{-8}

$$\left(\frac{F^\circ - H_0^\circ}{T}\right)_{\text{NiO solid}} = 84.360 - 0.415 \times 10^{-3}T - 31.523 \log T - (3465/T) + (1.46 \times 10^5/T^2) \quad (7)$$

For gaseous NiO we have used the equation

$$\left(\frac{F^\circ - H_0^\circ}{T}\right)_{\text{NiO gas}} = 3.5\,R - 3.5\,R \ln T - 1.5\,R \ln M - R \ln \mu - 2\,R \ln r_0 - 175.38 - R \ln q + R \ln (1 - e^{ch\nu/kT}) \quad (8)^{28}$$

with ν set equal to 700 wave numbers,[29] r_0 set equal to 1.65×10^{-8} cm.,[30] and q set equal to 3.[31]

The first two of these constants are necessarily estimates since no band spectra have been observed for nickel oxide. However, they are probably reliable to within 50 cm.$^{-1}$ in ν and to within 0.1 Å. in r_0. Combined errors of 50 cm.$^{-1}$ and 0.1 Å., respectively, would influence our calculations of ΔH_0° (Table VIII) by less than 600 calories in an absolute sense and would introduce a temperature trend into the supposed values of ΔH_0° of only 50 calories over the 130° experimental range. These are well within the limits of

TABLE VII

STANDARD FREE ENERGY FUNCTIONS OF NICKEL OXIDE (NiO) IN SOLID PHASE AND IN THE VAPOR (BASED ON THE SUPPOSITION THAT THE GROUND ELECTRONIC STATE OF NiO VAPOR IS $^3\Sigma$). CHANGE OF THE STANDARD FREE ENERGY FUNCTION IN EVAPORATION

T	$\left(\frac{F^\circ - H_0^\circ}{T}\right)_{\text{solid}}$	$\left(\frac{F^\circ - H_0^\circ}{T}\right)_{\text{vapor}}$	$\Delta\left(\frac{F^\circ - H_0^\circ}{T}\right)_{\text{evap.}}$
1000	−13.942	−57.420	−43.478
1100	−14.998	−58.195	−43.197
1200	−15.988	−58.907	−42.919
1300	−16.918	−59.567	−42.649
1400	−17.795	−60.183	−42.388
1500	−18.626	−60.763	−42.137
1600	−19.414	−61.306	−41.892
1700	−20.165	−61.815	−41.650
1800	−20.881	−62.292	−41.411
1900	−21.566	−62.745	−41.179
2000	−22.223	−63.182	−40.959

TABLE VIII

ΔH_0° FOR THE SUBLIMATION OF NICKEL OXIDE (NiO)

Run	T, °K.	4.575 $\log_{10} p$	ΔH_0° (q = 3)	ΔH_0° (q = 1)	ΔH° (q = 10)
6	1438	−39.41	117,489	*114,350*	*120,929*
5	1441	−39.71	118,156	*115,011*	*121,604*
7	1495	−36.16	117,070	*113,807*	*120,647*
4	1511	−34.66	115,997	*112,699*	*119,612*
2	1529	−34.61	117,233	*113,895*	*120,890*
1	1566	−32.35	116,386	*112,968*	*119,913*
Average ΔH_0° (±1000 cal.)			117,055	*113,789*	*120,635*

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(28) The first term in this equation is the contribution to $(H^\circ - H_0^\circ/T)$ arising from translation and rotation; the succeeding five terms constitute the sum of translational and rotational entropies for a rigid rotator of molecular weight M, reduced mass μ and internuclear distance r_0 [Sackur, *Ann. Phys.*, **36**, 958 (1911); Tetrode, *ibid.*, **38**, 434 (1921); Ehrenfest and Trkal, *Proc. Acad. Sci. Amsterdam*, **23**, 162 (1920)] the seventh term is the electronic contribution to $(F^\circ - H_0^\circ)/T$ from the multiplicity of the ground state; and the final term is the contribution from an harmonic oscillator with the fundamental frequency ν (expressed in wave numbers). R, c, h and k have their usual meaning.

(29) Our estimate of 700 cm.$^{-1}$ for the fundamental frequency of NiO is an interpolation within the group of transition elements of which nickel is a member. In order of increasing atomic number the series runs: TiO, 1007; VO, 1011; CrO, 896; MnO, 840; FeO, —; CoO, —; NiO, (700 est.); CuO, 620 cm.$^{-1}$ [*cf.* Herzberg, "Molecular Spectra," I, Table 36, Prentice-Hall, New York, N. Y., 1939]. Among the monochlorides and the hydrides nickel fits regularly into position: (a) TiCl, 456; VCl, —; CrCl, —; MnCl, —; FeCl, 406; CoCl, 420; NiCl, 418; CuCl, 417; ZnCl, 390; (b) MnH, 1580; FeH, —; CoH, 1890; NiH, 1926; CuH, 1940. (In some instances—*e. g.*, FeCl—these frequencies may not represent the ground electronic state.)

(30) Our estimate of 1.65 Å. for the covalent bond in NiO vapor is based on values for the atomic radius of nickel in various of its covalent compounds. We further assume the bond to be double (*cf.* ref. 31).

Pauling ["The Nature of the Chemical Bond," The Cornell University Press, 1939, p. 232] makes an estimate of about 1.22 Å. for the covalent single bond radius of nickel. A recent reliable determination of r_0 in the vapor of NiH [Heimer, Dissertation, Stockholm, 1937; *cf.* Herzberg, *loc. cit.*] yields 1.487 Å. for the Ni-H bond. Taking the H covalent radius to be 0.30 ± 0.03 Å. (Pauling, *loc. cit.*, p. 158) this gives 1.19 ± 0.03 Å. for the nickel single bond radius, in good agreement with the X-ray measurements. Use of the factor 0.915 for the double bond–single bond ratio (Pauling, *loc. cit.*, p. 154) yields 1.09 Å. for the double bond radius of nickel, and 1.66 Å. for r_0 in NiO vapor. This lies within the limits imposed by the results of electron diffraction measurements on the vapor of $Ni(CO)_4$ [Brockway and Cross, *J. Chem. Phys.*, **3**, 828 (1935); *cf.* also Pauling, *loc. cit.*, p. 232, *et seq.*]. These yield 1.82 Å. for the Ni–C bond, which resonates between single bond and double bond character, and result in extremes of 1.53 Å. and 1.72 Å. for the Ni–O double bond, with the most probable value near the upper limit.

(31) Professor R. S. Mulliken (private communication) expresses the opinion that the ground state of NiO is probably $^3\Sigma^-$, resulting from either the configuration Ni $d\sigma d\pi^3 d\delta^4 s\sigma^2$; O $p\sigma\ p\pi^3$ or Ni $d\sigma^2\ d\pi^3\ d\delta^4\ s\sigma$; O $p\sigma\ p\pi^3$, or a mixture, and that the Ni–O bond would be expected to exhibit properties similar to the double bond in molecular oxygen. The multiplicity (q) of the $^3\Sigma$ state would be 3. It is possible, though less likely that $^1\Sigma^+$ (with q = 1) would be more stable than $^3\Sigma^-$ (analogy to the possible situation in Se^2 and Te^2). Less probable multiplicities are 2, 5, 6 or 10.

error imposed by the measurements of sublimation rates of nickel oxide, and would not alter their interpretation.

Values of the free energy function, computed by equation (7) for solid nickel oxide and by equation (8) for the vapor, are given in Table VII, together with $\Delta(F^\circ - H_0^\circ)/T$ for the sublimation process. The latter is well represented, empirically, by the equation

$$\left(\frac{F^\circ - H_0^\circ}{T}\right)_{\text{NiO (gas)}} - \left(\frac{F^\circ - H_0^\circ}{T}\right)_{\text{NiO (solid)}} = -46.656 + 3.508 \times 10^{-3}T - 3.30 \times 10^{-7}T^2 \quad (9)$$

Values for the sublimation heat at the absolute zero, based on $^3\Sigma^-$ as the probable ground state of nickel oxide vapor, are given in the fourth column of Table VIII. These are computed by combination of equations (2) and (9) with the experimental pressures recorded in Table VI.

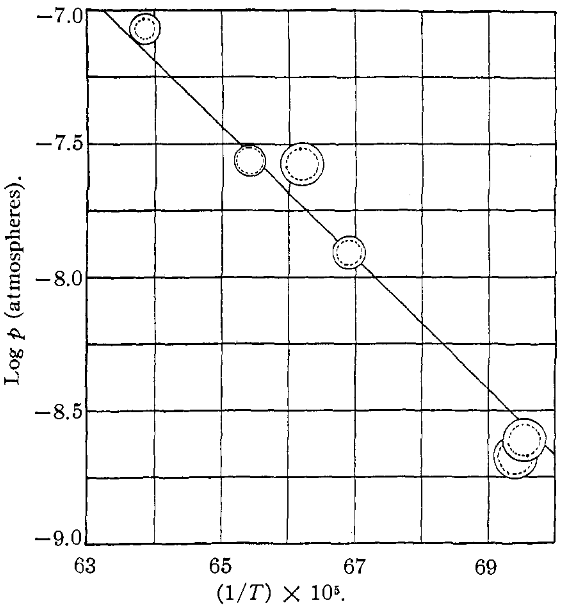

Fig. 2.—Vapor pressures of nickel oxide. The dimensions of the outer (solid line) circles are drawn to scale to represent approximate error limits. The inner (broken line) circles represent probable errors. The curve is constructed from equation (10).

Substitution of the average value for ΔH_0° (117,055) into equation (2), in combination with equation (9), leads to the vapor pressure equation

$$\log p \text{ (atmospheres)} = -\frac{25{,}586}{T} - 7.67 \times 10^{-4}T + 7.21 \times 10^{-8}T^2 + 10.198 \quad (10)$$

The fit with the individual experimental data is shown graphically in Fig. 2, in which the curve is constructed from equation (10). Approximate error *limits* of the individual data are represented by the dimensions of the outer (full line) circles and their *probable* errors by the inner (broken line) circles.[32]

Although 3 is the most likely value for q in equation (8) extreme limits of 1 and of 10 are not definitely excluded (*cf.* ref. 31). Accordingly, we include in Table VIII columns (italics) based on these extreme assignments. When allowance is made for the added small uncertainties from r_0 and from ν and from an experimental uncertainty of 1000 calories in the average of ΔH_0° for a single column, it is seen that the total uncertainty in ΔH_0° may attain 4 to 5 kilocalories as a limit. A "best" straight line drawn among the experimental points, as in graphic treatment by the Clausius–Clapeyron equation, yields about 127 kilocalories for ΔH_{1500°, which is equivalent to about 132 kilocalories for ΔH_0°. However, the slope of this line may be varied, within the limits of error of the data, by an amount that corresponds to nearly ±15 kilocalories in ΔH_0°. Hence, even with the possibility of a four kilocalorie error in the estimates of r_0, ν and of q the thermodynamic treatment represented in equations (2), (7) and (8) is markedly superior to treatment by the Clapeyron equation, for the purpose of smoothing up vapor pressure data, or of computing ΔH_0°.

Evidence against the Presence of Dissociation.—The preceding kinetic and thermodynamic treatment for nickel oxide is based on the supposition that sublimation as nickel oxide represents the only mechanism by which oxygen escapes from the oxide film during the process of evaporation. The good agreement of ΔH_0° among the several runs (Table VIII) substantiates this treatment. However, in view of the conflicting values reported in the literature for nickel oxide dissociation pressures[33] (some being higher, at 1500°,

[32] The error limits for NiO are considerably greater than for nickel (Fig. 1) due to the small evaporation losses of oxygen (on which the evaporation losses of NiO are based) and to the fact that these must be computed as differences between four weighings (each uncertain to ±0.02 mg. (*cf.* Table V). The error *limits* were arrived at by combining arithmetically the error from ±3° uncertainty in temperature with a 0.05 mg. probable error from accumulation of four weighing errors. The *probable* errors of the plotted points are computed from the usual probable error formula for addition or subtraction of chance errors, namely, P. E. = $\sqrt{\Sigma e^2}$, and make allowance for the chance that temperature and weighing errors may be of opposite sign.

[33] Foote and Smith, THIS JOURNAL, **30**, 1344 (1908); Pease and Cook, *ibid.*, **48**, 1199 (1926); Wohler and Balz, *Z. Elektrochem.*, **37**, 406 (1931); Skapsky and Dabrowsky, *ibid.*, **38**, 365 (1932); Kapustinsky and Shamovsky, *Z. anorg. allgem. Chem.*, **216**, 10 (1933). *Cf.* also Emmett and Schultz, THIS JOURNAL, **52**, 4268 (1930). Our own observation that free nickel readily passes through the oxide films (*cf.* Tables V and X) raises serious doubt as to the validity of the experimental method employed by Kapustinsky and Shamovsky.

TABLE IX

DISSOCIATION PRESSURES OF NiO

T, °K.	1440	1495	1511	1529	1566
p (mm. of O_2)	5.9×10^{-7}	2.5×10^{-6}	3.8×10^{-6}	5.6×10^{-6}	1.4×10^{-8}

than the residual gas pressure in our apparatus) we have given special consideration to the alternative mechanism of nickel oxide decomposition into nickel and free oxygen.

Direct evidence that dissociation was not taking place was provided by a micro-determination[34] of the gases pumped off continuously and collected, during one of the runs. No measurable trace of oxygen was present. Had decomposition into nickel and free oxygen been the evaporation mechanism the order of 0.5 cc. of oxygen (N. T. P.) would have been liberated. While some of this would unquestionably react with the fresh nickel film which formed on the walls of the cell (*cf. seq.*), it does not appear plausible that no trace would reach the pump, out of such a relatively large sample.

The conclusion to be drawn from this evidence is also confirmed by a calculation of dissociation pressures which can now be made from the thermodynamic data for nickel (Table II), for nickel oxide (Table VII), and that for oxygen[35] in conjunction with Roth's[36] thermochemical value of -58.9 kilocalories for the standard ΔH of formation of solid nickel oxide from its elements at 25°. These data yield the following oxygen pressures (Table IV) for dissociation at the respective temperatures of our runs.

Consideration of the ($O_2 = 2\ O$) equilibrium[35] at these temperatures and O_2 pressures yields the result that the partial pressures of monatomic oxygen are negligible in comparison.

The pressures in Table IX lie below the residual pressure of gas in our apparatus, with the possible exception of the 1566° run. Therefore, we can definitely eliminate dissociation for any of the runs in the lower range of temperature. Furthermore, if dissociation occurred at significant rate in either the 1566 or 1529° runs, these runs would have been attended with an abnormally high loss of oxygen and we would have computed correspondingly low values for ΔH_0°. Actually, no significant variation was observed among the values for ΔH_0° (*cf.* Table VIII). Thus we may conclude that dissociaton cannot have occurred with any of the runs by amounts that can be regarded as significant in the data.

Evaporation of Nickel.—It is interesting to observe that the evaporation of free nickel is almost as great as it would be in the absence of the oxide film and that there is little correlation between nickel evaporation and the film thickness. This is brought out in Table X. In general, it does appear that very thick films of oxide permit more rapid escape of nickel than do thin films. This may be the result of mechanical breakage of the film in the process of heating up the coated rings or in the escape of dissolved oxygen during evacuation.

TABLE X

EVAPORATION OF NICKEL THROUGH A FILM OF NiO

Run	T, °K.	Film thickness, Å.	Nickel evaporation, g.		
			Calcd. for pure Ni	Obsd.	% of calcd.
6	1438	70,000	0.0149	0.0153	100 (+)
5	1441	38,000	.0161	.0099	61
7	1495	92,000	.0191	.0148	78
4	1511	46,000	.0072	.0028	39
2	1529	50,000	.0218	.0075	35
1	1566	21,000	.0265	.0119	45

Summary

Rates of evaporation of solid nickel have been measured between approximately 1300 and 1600°K., and the data employed to compute vapor pressures of the metal. The results obtained are in good agreement with thermodynamic requirements for the free energy of evaporation and yield 101,141 (±150) calories for the heat of sublimation at the absolute zero. The data yield the accurate vapor pressure equation, for solid nickel

$$\log p \text{ (atmospheres)} = -\frac{22,107}{T} - 1.31 \times 10^{-4}T + 7.869$$

Comparisons are made with earlier data by Jones, Langmuir and Mackay, and by Bryce, who measured evaporation rates from thin nickel filaments.

The accommodation coefficient for the condensation of nickel vapor on the equilibrium surface is unity within the experimental limits of accuracy and cannot lie below 0.75 as a lower limit.

Vapor pressures of nickel oxide (NiO) also have been determined, for the temperature interval 1440 to 1566°K., by measurement of the evapora-

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(34) F. J. Norton and A. L. Marshall, *Trans. Am. Inst. Mining Met. Eng.*, **102**, 287 (1932); Langmuir, THIS JOURNAL, **35**, 105 (1913).

(35) H. L. Johnston and M. K. Walker, *ibid.*, **55**, 172, 187 (1933); *ibid.*, **57**, 682 (1935).

(36) Roth, *Z. angew. Chem.*, **42**, 981 (1929).

tion losses from oxide films coated on nickel rings. While less accurate than the data for nickel, the results are in agreement with the thermodynamic requirements for evaporation of nickel oxide, and yield 117,055 (±1000) calories for the heat of sublimation at the absolute zero. Allowance for some uncertainty in the ground state multiplicity of NiO vapor, and in molecular constants, increases the possible error limit by three to four kilocalories. The data yield the vapor pressure equation

$$\log p \text{ (atmospheres)} = -\frac{25{,}506}{T} - 7.67 \times 10^{-4}T + 7.21 \times 10^{-8}T^2 + 10.198$$

Absence of oxygen in the gases pumped from the sample during evaporation, and a comparison of the residual gas pressures in our apparatus with the dissociation pressures of NiO within the temperature range of our measurements, exclude any significant influence from NiO dissociation.

Evaporation of free nickel was little retarded by the presence of the oxide coatings ranging from 20,000 to 90,000 Å. in thickness.

Recent data on the heat capacity of nickel have been reviewed and values for the heat content, entropy and free energy function have been computed and tabulated. Tables of the free energy functions of NiO (solid) and NiO (vapor) are also included.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Vapor Pressures of Salt Solutions[1]

BY MAX F. BECHTOLD[2] AND ROY F. NEWTON

A convenient and accurate method for measuring the activities of water in salt solutions is very desirable in those cases in which it is difficult or impossible to obtain satisfactory measurements of the activities of the solute by electromotive force measurements. The method of Washburn and Heuse[3] modified by Gibson and Adams[4] and by Newton and Tippetts[5] appears to be quite promising, and has been further modified to increase both its accuracy and its convenience. Essentially the method consists of passing a gas successively through saturators containing pure water, an absorber, saturators containing the solution, and finally through a second absorber. Passing the same gas through both the pure water and the solution eliminates the need of measuring the gas. The vapor pressure of the solution can then be expressed simply in terms of the vapor pressure of pure water, the total pressure at each saturator, and the gain in weight of each absorber. In the older apparatus the pressure at the saturators varied, and it was necessary to read the pressures at frequent intervals during long runs in order to obtain reliable averages. The adaptation of relays for controlling the discharge pressure and the rate of passage of gas through the apparatus has made necessary only a single reading of each pressure. Slight condensation in the tubes connecting the saturators with the absorbers may produce serious uncertainties in the results, which has been obviated by enclosing the absorbers and connecting tubes in an air-bath just above the water-bath, maintained about five degrees higher than the latter, and at high humidity, thus preventing cooling due to evaporation at the point where the connecting tubes leave the water-bath. During preliminary adjustments the air-bath must be removed, and condensation may then occur in the connecting tubes. To avoid error due to collecting this condensate in the absorbers, a pair of "dummy" absorbers is connected in parallel with the weighed ones, and the gas is passed through them for about an hour after the air-bath has been adjusted. The establishment of steady flow conditions before the collection of water in the weighed absorbers also ensures that the same quantity of gas passes through both absorbers.

Apparatus and Materials

Measurements were made on solutions of barium chloride and of calcium chloride. The barium chloride solutions were prepared and analyzed as reported by Newton and Tippetts.[5] A sample of Mallinckrodt Analytical

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[1] Based upon a thesis submitted by Max F. Bechtold to the Faculty of Purdue University in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1939. Presented at the Boston meeting of the American Chemical Society, September, 1939.

[2] Present address: du Pont Experimental Station, Wilmington, Delaware.

[3] Washburn and Heuse, THIS JOURNAL, **37**, 309 (1915).

[4] Gibson and Adams, *ibid.*, **55**, 2679 (1933).

[5] Newton and Tippetts, *ibid.*, **58**, 280 (1936).