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# Saturated Vapour Pressure and Enthalpy of Sublimation of Nickel

**Valerii I. Severin,*[a] Alla V. Tseplayaeva,[a] Nonna E. Khandamirova,[b] Yurii A. Priselkov,[a] Natalya A. Chernova,[a] Iten V. Golubtsov[a] and Valerii B. Luk'yanov[a]**

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119898 Moscow, Russian Federation.*
*Fax: +7 095 939 0126*
[b] *Institute of High Temperatures, Russian Academy of Sciences, 127412 Moscow, Russian Federation*

The vapour pressure of nickel has been determined over the temperature range 1522–1793 K.

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It is possible to obtain unequivocal information on the vapour pressure and enthalpy of sublimation of nickel, despite a number of available sources (see Table 1). This circumstance resulted in our present work, investigating the evaporation of nickel. We have tried to exclude, as far as possible, the sources of errors present in previous work.

The temperature dependence of the vapour pressure of nickel has been determined by means of an integral variant of the Knudsen method in a hydrocarbon-free vacuum ($10^{-6}$–$10^{-7}$ Pa). The principles of the operation and design of the device are described elsewhere.[14] The effusion cell and diaphragm (the size of the diaphragm is given in Table 2) were

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**Table 1** Enthalpy of sublimation of nickel at 298.15 K according to data obtained by various authors[a]

| Author, ref. (year) | Method | No. of measurements | Temp. range $T$/K | Enthalpy of sublimation at 298.15 K/kJ mol$^{-1}$ 2nd Law | Enthalpy of sublimation at 298.15 K/kJ mol$^{-1}$ 3rd Law |
|---|---|---|---|---|---|
| Jones, 1 (1927) | Langmuir | 5 | 1318–1602 | 377 ± 93 | 409.6 ± 5.9 |
| Bryce, 2 (1936) | Langmuir | Equation | 1250–1425 | 390 | 420.2 ± 25 |
| Johnston, 3 (1940) | Langmuir | 12 | 1307–1583 | 429 ± 8 | 423.8 ± 0.5 |
| Morris, 4 (1957) | Carrier gas | 16 | 1816–1895 | 434 ± 11 | 429.8 ± 0.1 |
| Nesmeyanov, 5 (1960) | Knudsen | 11 | 1320–1550 | 362 ± 16 | 337.8 ± 1.1 |
| Grimley, 6 (1961) | Knudsen | 16 | 1575–1709 | 472 ± 11 | 426.2 ± 0.6 |
| Kovtun, 7 (1962) | Open crucible | 13 | 1462–1639 | 501 ± 33 | 425.0 ± 2.0 |
| Vrestal, 8 (1971) | Knudsen | 19 | 1444–1593 | 436 ± 18 | 421.7 ± 0.5 |
| Rutner, 9 (1974) | Langmuir | 28 | 1233–1658 | 406 ± 67 | 431.7 ± 4.8 |
| Pozhidaev, 10 (1974) | Langmuir | 44 | 1723–1973 | 413 ± 26 | 433.6 ± 1.2 |
| Bochkova, 11 (1981) | Knudsen | 5 | 1573–1713 | 441 ± 9 | 423.3 ± 0.8 |
| Bodrov, 12 (1982) | Atomic absorption | 23 | 1489–1708 | 424 ± 12 | 419.8 ± 2.0 |
| | | 9 | 1823–2110 | 418 ± 32 | 419.0 ± 1.2 |
| Bobler, 13 (1985) | Boiling point | 1 | 3160 | | 430.2 |

[a] Table 1 gives the results of fundamental investigations on the vapour pressure of nickel.

made from alumina and were degassed *in vacuo* before use. Samples of nickel of 99.99% and 99.96% purity and a sample of the radioisotope nickel-63 were used. The amount of evaporated nickel was determined by a colorimetric method[15] and by isotopic dilution with a substoichiometric discharge of diethyl dithiocarbamatonickel(II). The saturated vapour pressure of nickel was calculated according to eqn. (1), where $P$ is the

$$P = m(K\sigma\tau)^{-1}(2\pi RTM^{-1})^{1/2} \qquad (1)$$

vapour pressure, $m$ the mass of substance being evaporated, $\sigma$ is the area of the effusion orifice, $K$ is Clausings' factor, $\tau$ is the evaporation time, $M$ is the molecular weight of nickel vapour and $T$ the temperature, (other symbols have their conventional meanings). The results obtained are given in Tables 2 and 3 and Fig. 1.

In order to test whether equilibrium was established in the Knudsen cell the experiments were carried out using nickel samples with various surface evaporation areas (powder, foil, smelted powder, liquid) using the same effusion orifice. The results obtained were treated using the least-squares method and the temperature dependence of the vapour pressures of liquid and solid nickel were calculated. Statistical analysis [16,17] revealed the statistical equivalence of the results for the vapour pressure of solid nickel which were obtained in all the experimental series. The results did not depend on the area and state of the evaporation surface. This allowed us to calculate an overall regression equation for the vapour pressure of solid nickel (Table 3). The enthalpy of sublimation of nickel at 298.15 K was calculated in accordance with the second and third laws of thermodynamics using IVTANTERMO† thermodynamic functions† for solid and liquid nickel (Table 3). The statistical equivalence of the values of the enthalpy of sublimation of nickel at 298.15 K calculated from the vapour pressure of liquid and solid nickel was demonstrated, and a value of $\Delta_{sub}H^{\circ}$ (Ni, cr, 298.15 K) = 424.7 ± 0.3 kJ mol$^{-1}$ was obtained. It follows from Table 1 that this value agrees with those for the enthalpy of sublimation of nickel calculated in refs. 3, 11 (within the limits of experimental error) but differs from the other values given in Table 1. The data on the vapour pressure of liquid nickel obtained in the present work are different from those in the literature. In our view the reason for the lower values obtained for the vapour pressure of nickel is the existence of unvolatilied films on the surface of the evaporated sample. These films are generated by the interaction of nickel with the material of the effusion cell. Apparently, larger values of the vapour pressure of nickel result from the use of an effusion cell made from molybdenum that interacts with the nickel.[18] Moreover, nickel can diffuse through the molybdenum diaphragm, causing an increase of the nickel content in the condensate.

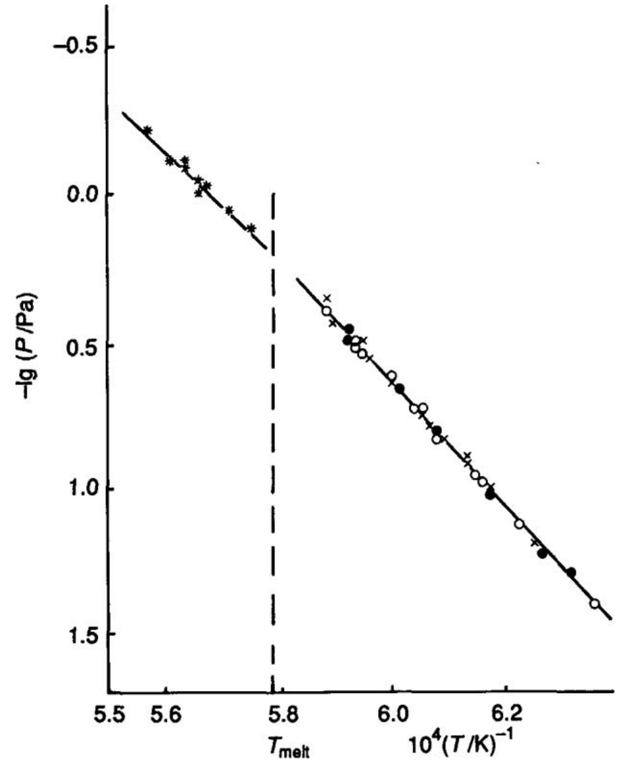

**Fig. 1** Temperature dependence of the vapour pressure of nickel (×) foil (containing radioisotope $^{63}$Ni), (○) smelted powder, (●) powder, (*) liquid nickel

We consider that the data on the vapour pressure and enthalpy sublimation of nickel presented here is the most reliable available for the following reasons. (*i*) The experiments were performed in ultra-high oilless vacuum using samples of high purity nickel. (*ii*) The data on the vapour pressure of various samples (powder, smelted powder, foil) of solid nickel are statistically equivalent. (*iii*) The values of the enthalpy of sublimation of nickel at 298.15 K calculated by the second and third laws of thermodynamics are in good agreement with one another. (*iv*) The values of the enthalpy of sublimation of nickel

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† Thermodynamic functions were provided by the Thermocentre of the Russian Academy of Sciences.

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**Table 2** Experimental data on vapour pressure and corresponding third-law enthalpy of sublimation for nickel at 298.15 K[a]

| No. | Temp. $T$/K | Evaporation time $\tau$/s | Mass of condensate $10^9$ ($m$/kg) | Vapour pressure ($P$/Pa) | $\Delta_{\text{sub}}H^{\circ}$ (Ni, cr, 298.15 K)/kJ mol$^{-1}$ |
|---|---|---|---|---|---|
| Series 1[b] | | | | | |
| 1 | 1666 | 1800 | 850 | 2.201 | 424.691 |
| 2 | 1666 | 1500 | 710 | 2.196 | 424.724 |
| 3 | 1583 | 1800 | 185 | 0.465 | 424.526 |
| 4 | 1583 | 1815 | 187 | 0.467 | 424.493 |
| 5 | 1621 | 1800 | 352 | 0.897 | 425.626 |
| 6 | 1621 | 1860 | 366 | 0.903 | 425.542 |
| 7 | 1642 | 1200 | 370 | 1.424 | 424.691 |
| 8 | 1642 | 1200 | 381 | 1.465 | 424.290 |
| 9 | 1663 | 900 | 400 | 2.065 | 424.830 |
| 10 | 1663 | 900 | 386 | 1.993 | 425.324 |
| 11 | 1686 | 900 | 550 | 2.858 | 425.983 |
| 12 | 1688 | 900 | 645 | 3.354 | 424.230 |
| Series 2[c] | | | | | |
| 13 | 1572 | 1800 | 150 | 0.376 | 424.436 |
| 14 | 1604 | 1200 | 201 | 0.760 | 423.481 |
| 15 | 1627 | 900 | 206 | 1.040 | 425.006 |
| 16 | 1627 | 900 | 205 | 1.037 | 425.072 |
| 17 | 1646 | 960 | 319 | 1.488 | 425.092 |
| 18 | 1647 | 900 | 295 | 1.485 | 425.098 |
| 19 | 1669 | 900 | 435 | 2.249 | 425.132 |
| 20 | 1669 | 900 | 435 | 2.249 | 425.132 |
| 21 | 1522 | 2600 | 70 | 0.120 | 425.761 |
| 22 | 1522 | 1560 | 50 | 0.143 | 423.554 |
| 23 | 1640 | 600 | 187 | 1.429 | 424.049 |
| 24 | 1640 | 600 | 184 | 1.415 | 424.269 |
| 25 | 1685 | 600 | 386 | 3.009 | 425.022 |
| 26 | 1686 | 620 | 420 | 3.169 | 424.539 |
| 27 | 1622 | 1800 | 394 | 1.004 | 424.358 |
| 28 | 1622 | 1800 | 388 | 0.989 | 424.565 |
| 29 | 1647 | 1230 | 417 | 1.568 | 424.628 |
| 30 | 1647 | 1200 | 403 | 1.553 | 424.758 |
| 31 | 1657 | 2360 | 895 | 1.759 | 425.551 |
| 32 | 1681 | 600 | 391 | 3.044 | 423.878 |
| 33 | 1697 | 900 | 726 | 3.786 | 424.721 |
| 34 | 1697 | 900 | 720 | 3.754 | 424.838 |
| Series 3[d] | | | | | |
| 35 | 1595 | 1200 | 168 | 0.637 | 423.515 |
| 36 | 1595 | 1200 | 165 | 0.625 | 423.754 |
| 37 | 1621 | 900 | 215 | 1.096 | 422.929 |
| 38 | 1641 | 925 | 316 | 1.577 | 423.045 |
| 39 | 1661 | 900 | 427 | 2.202 | 423.440 |
| 40 | 1679 | 900 | 572 | 2.968 | 423.746 |
| 41 | 1697 | 600 | 558 | 4.365 | 422.714 |
| 42 | 1697 | 865 | 735 | 3.988 | 423.988 |
| 43 | 1678 | 1680 | 1057 | 2.936 | 423.645 |
| 44 | 1662 | 900 | 450 | 2.322 | 422.959 |
| 45 | 1646 | 900 | 360 | 1.849 | 422.119 |
| 46 | 1626 | 910 | 250 | 1.263 | 422.289 |
| 47 | 1595 | 1850 | 260 | 0.640 | 423.464 |
| Series 4[e] | | | | | |
| 48 | 1741 | 300 | 470 | 7.447 | 425.478 |
| 49 | 1742 | 480 | 738 | 7.311 | 425.947 |
| 50 | 1764 | 300 | 645 | 10.29 | 425.969 |
| 51 | 1765 | 300 | 644 | 10.28 | 426.212 |
| 52 | 1778 | 300 | 802 | 12.84 | 425.831 |
| 53 | 1778 | 300 | 810 | 12.97 | 425.685 |
| 54 | 1793 | 300 | 1004 | 16.14 | 425.754 |
| 55 | 1760 | 310 | 637 | 9.821 | 425.759 |
| 56 | 1760 | 1230 | 2413 | 9.377 | 426.428 |
| 57 | 1767 | 900 | 1894 | 10.08 | 426.945 |
| 58 | 1749 | 612 | 1051 | 8.182 | 425.930 |

[a] In series 1–4 the diameter of the effusion orifice is 0.236 cm, the thickness is 0.164 cm, $K = 0.599$ and the value $K\delta = 2.620 \times 10^{-2}$. [b] Solid: nickel (99.99% pure) powder annealed in a hydrogen stream. [c] Solid: nickel (99.99% pure) powder annealed in a hydrogen stream and smelted *in vacuo*. [d] Solid: nickel (99.96% pure) foil containing radioisotope $^{63}$Ni. [e] Liquid: nickel (99.99% pure).

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**Table 3** Constants for eqns. (2) and (3) for the temperature dependence of the saturated vapour pressure of nickel, $\lg P = (A \pm \Delta A) - (B \pm \Delta B)T^{-1}$ and values of the enthalpy of sublimation at 298.15 K for nickel

| No. | Ni sample | Temp. range $T$/K | No. of measurements $n$ | $A \pm \Delta A$ | $B \pm \Delta B$ | $\Delta_{sub}H^\circ$ (Ni, cr, 298.15 K)/kJ mol$^{-1}$ 2nd Law | 3rd Law |
|---|---|---|---|---|---|---|---|
| 1 | Powder | 1583–1688 | 12 | 12.17 ± 0.60 | 21 400 ± 940 | 421 ± 18 | 424.9 ± 0.4 |
| 2 | Smelted powder (99.99% pure) | 1522–1697 | 22 | 12.22 ± 0.30 | 21 450 ± 470 | 422 ± 9 | 424.6 ± 0.3 |
| 3 | Foil, containing $^{63}$Ni | 1595–1697 | 13 | 12.26 ± 0.53 | 21 460 ± 870 | 422 ± 17 | 423.2 ± 0.4 |
| 4 | Solid Ni | 1522–1697 | 47 | 12.27 ± 0.33 | 21 530 ± 540 | 423 ± 10 | 424.3 ± 0.3 |
| 5 | Liquid Ni | 1741–1793 | 11 | 11.68 ± 1.01 | 20 600 ± 1800 | 425 ± 34 | 426.0 ± 0.3 |
| 6[b] | Solid and liquid Ni | 1522–1793 | 58 | — | — | — | 424.7 ± 2.0 |

[a] Corresponding absolute errors are given by 0.95 confidence limits. [b] Series 6 takes account of errors in the thermodynamic functions.

at 298.15 K calculated from the experimental results on the vapour pressure of solid and liquid nickel are statistically equivalent. Facts (*i*)–(*iv*) allow us to propose equations (2) and (3) for the temperature dependence of the vapour pressure of

$$\lg P(\mathrm{s})/\mathrm{Pa} = (12.27 \pm 0.33) - (21\,530 \pm 540)T^{-1} \quad (1522\text{–}1697\ \mathrm{K}) \qquad (2)$$

$$\lg P(\mathrm{l})/\mathrm{Pa} = (11.68 \pm 1.01) - (20\,600 \pm 1800)T^{-1} \quad (1741\text{–}1793\ \mathrm{K}) \qquad (3)$$

nickel (errors are given by 0.95 confidence limits) and the value obtained is $\Delta_{sub}H^\circ$ (Ni, cr, 298.15 K) = 424.7 ± 2.0 kJ mol$^{-1}$. (The uncertainties of the thermodynamic functions are taken into account.)

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