

Thermodynamic Functions of Nickel Carbonyl and Iron Pentacarbonyl

L. W. ROSS, F. H. HAYNIE, and R. F. HOCHMAN
Georgia Institute of Technology, Atlanta, Ga.

THERMODYNAMIC FUNCTIONS of nickel carbonyl and iron pentacarbonyl are calculated using recent spectroscopic data and assuming the rigid rotator harmonic oscillator approximation. The functions C_p° , S° , $(H^\circ - H_0^\circ)$, and $-(F^\circ - H_0^\circ)/T$ are calculated at 298.15° K. and at 100° intervals from 300° K. to 1500° K. Equations relating equilibrium constant to temperature for the formation of these compounds from carbon monoxide and the metal are derived, using the calculated thermodynamic functions.

NICKEL CARBONYL

Stammreich and his coworkers (19) have observed that the vibrational spectra of nickel carbonyl are the most thoroughly investigated of all metal carbonyls. The Raman spectra determined by Stammreich and his coworkers, and the Raman and infrared spectra determined by Bigorgne and Chelkowski (2) and Jones (11) have made possible the calculation of ideal gas thermodynamic properties for this compound with an accuracy unavailable for other metal carbonyls.

In the present work the thermodynamic functions C_p° , S° , $(H^\circ - H_0^\circ)$, and $-(F^\circ - H_0^\circ)/T$ have been calculated at 298.15° K. and at 100° intervals from 300° to 1500° K., using the rigid rotator harmonic oscillator approximation. The frequencies assigned by Stammreich and coworkers (19) have been used for this calculation, with a symmetry number of 12, and a value of 5.38×10^{-112} gm.³cm.⁶ for the moment of inertia product as determined by Bigorgne (3). This value for the moment of inertia is more reliable than the value of 5.03×10^{-112} gm.³cm.⁶ used by Crawford and Cross (7) in their classic work on nickel carbonyl, and agrees well with the value of $(5.25 \pm 0.3) \times 10^{-112}$ gm.³cm.⁶ calculated by Kipnis (13).

In Table I are shown the results, obtained by computation on a Burroughs 220 digital computer. In Table II the values of S° , C_p° , and $-(F^\circ - H_0^\circ)/T$ calculated at 298.15° K. using frequency assignments according to several investigators are compared with the third-law entropy obtained calorimetrically by Spice and coworkers (18). The calorimetric value, however, is admittedly subject to error.

The thermodynamic equilibrium constant of the reaction $\text{Ni}(s) + 4\text{CO}(g) = \text{Ni}(\text{CO})_4(g)$ may now be determined as

a function of temperature. The standard free energy is related to the temperature by:

$$\Delta F^\circ = \Delta H^\circ + T\Delta S^\circ \quad (1)$$

and the equilibrium constant is given by:

$$\log_{10} K_e = -\frac{\Delta F^\circ}{2.3026RT} = -\frac{\Delta H^\circ}{2.3026RT} + \frac{\Delta S^\circ}{2.3026R} \quad (2)$$

The standard heat of reaction at 25° C. has been established by Fischer, Cotton, and Wilkinson (10) as -39.1 kcal./mole. This value seems to have been overlooked by Kipnis (13) who chose -37.2 kcal./mole as the most probable value. Using standard sources (21) for thermodynamic functions of the reactants with the data of the present work for nickel carbonyl, the equation:

$$\log_{10} K_e = 8546/T - 21.64 \quad (3)$$

is obtained at 25° C. The equation obtained by Kipnis (13) is:

$$\log_{10} K_e = 8130(\pm 390)/T - (21.90 \pm 0.04) \quad (4)$$

Kipnis has plotted $\log_{10} K_e$ vs. $1/T$ as reported by a number of early investigators, and most of these data predict a lower value of K than either Equation 2 or Equation 4.

Table II. Comparison of Thermodynamic Functions of Nickel Carbonyl Determined from Various Sources

| Source | C_p° _{298.15} | S° _{298.15} | $-(F^\circ - H_0^\circ)/T$ _{298.15} |
|--|-------------------------------|-----------------------------|--|
| Crawford and Cross (7) | 34.8 | 97.0 | 73.4 |
| Bigorgne (3) | ... | 97.1 | 73.6 |
| Bigorgne (2) | ... | 99.8 | ... |
| This work ^a | 34.6 | 98.2 | 74.6 |
| This work ^b | 34.5 | 96.2 | 73.1 |
| This work ^c | 35.3 | 97.7 | 73.8 |
| Calorimetric [Spice, Stavely, and Harrow (18)] | ... | 95.4 | ... |

^a Calculated using frequency assignments of Stammreich and coworkers (19). ^b Calculated using frequency assignments of Jones (11) and Bigorgne (2) as suggested by Kipnis (13). ^c Calculated using frequency assignments of Jones (11).

Table I. Thermodynamic Functions of Nickel Carbonyl Ideal Gas

| Temp., ° K. | C_p° Cal./Mole ° K. | S° Cal./Mole ° K. | $(H^\circ - H_0^\circ)$ Cal./Mole | $-(F^\circ - H_0^\circ)/T$ Cal./Mole ° K. |
|-------------|-------------------------------|-----------------------------|--------------------------------------|--|
| 298.15 | 34.6 | 98.2 | 7064.9 | 74.6 |
| 300 | 34.7 | 98.5 | 7128.7 | 74.7 |
| 400 | 37.6 | 108.9 | 10758.5 | 82.0 |
| 500 | 38.5 | 117.5 | 14620.8 | 88.3 |
| 600 | 41.0 | 124.8 | 18650.7 | 93.8 |
| 700 | 42.2 | 131.3 | 22816.7 | 98.7 |
| 800 | 43.3 | 137.0 | 27096.8 | 103.1 |
| 900 | 44.1 | 142.1 | 31472.8 | 107.2 |
| 1000 | 44.9 | 146.8 | 35929.2 | 110.9 |
| 1100 | 45.5 | 151.1 | 40452.7 | 114.4 |
| 1200 | 46.0 | 155.1 | 45032.4 | 117.6 |
| 1300 | 46.4 | 158.8 | 49659.3 | 120.6 |
| 1400 | 46.8 | 162.3 | 54325.9 | 123.5 |
| 1500 | 47.1 | 165.5 | 59026.1 | 126.2 |

Table III. Thermodynamic Functions of Iron Pentacarbonyl Perfect Gas

| Temp., ° K. | C_p° Cal./Mole ° K. | S° Cal./Mole ° K. | $(H^\circ - H_0^\circ)$ Cal./Mole | $-(F^\circ - H_0^\circ)/T$ Cal./Mole ° K. |
|-------------|-------------------------------|-----------------------------|--------------------------------------|--|
| 298.15 | 40.7 | 105.0 | 7907.7 | 78.5 |
| 300 | 40.8 | 105.3 | 7983.2 | 78.7 |
| 400 | 45.2 | 117.7 | 12301.1 | 86.9 |
| 500 | 48.0 | 128.1 | 16967.3 | 94.1 |
| 600 | 50.2 | 137.0 | 21881.7 | 100.6 |
| 700 | 51.9 | 144.9 | 26991.3 | 106.3 |
| 800 | 53.4 | 151.9 | 32260.0 | 111.6 |
| 900 | 54.6 | 158.3 | 37659.5 | 116.5 |
| 1000 | 55.5 | 164.1 | 43166.5 | 120.9 |
| 1100 | 56.3 | 169.4 | 48762.2 | 125.1 |
| 1200 | 57.0 | 174.4 | 54431.3 | 129.0 |
| 1300 | 57.6 | 179.0 | 60161.4 | 132.7 |
| 1400 | 58.0 | 183.2 | 65942.7 | 136.1 |
| 1500 | 58.4 | 187.3 | 71766.9 | 139.4 |

Table IV. Comparison of Thermodynamic Functions of Iron Pentacarbonyl Determined from Various Sources

| Source | $C_p^{298.15}$ | $S_{298.15}$ | $-(F^\circ - H_8)_{298.15}/T$ |
|---|----------------|--------------|-------------------------------|
| King and Lippincott (12) ^a | 41.6 | 104.3 | 77.5 |
| Murata and Kawai (16) | ... | 102.6 | ... |
| Edgell and Wilson (9) | ... | 106.1 | ... |
| O'Dwyer (17) ^b | 40.8 | 105.1 | 78.5 |
| This work ^c | 39.3 | 103.5 | 77.9 |
| This work ^d | 40.7 | 105.0 | 78.5 |
| Leadbetter and Spice (14) ^e | ... | 106.0 | ... |
| Calorimetric [Leadbetter and and Spice (14)] | ... | 106.4 ± 0.8 | ... |

^aCorrected values due to Leadbetter and Spice (14). ^bCalculated in the present work, using O'Dwyer's frequency assignments, based on the tetragonal pyramid model. ^cCalculated using frequency assignments of Stammreich et al. (20), McDowell and Jones (15),

and Bor (4). ^dCalculated as before, with ν_{16} as assigned by King and Lippincott (12). ^eCalculated using frequency assignments of King and Lippincott (12) as modified by results of Cotton et al (5).

The aggregate data is well fitted by the equation of Tomlinson (22):

$$\log_{10}K_a = 6988/T - 19.22 \quad (5)$$

As pointed out by Spice, Stavely, and Harrow (18), the difficulty seems to lie in the state of the solid nickel in the reaction.

IRON PENTACARBONYL

The vibrational spectra of iron pentacarbonyl are not so well established as those of nickel carbonyl. Until recently there has been some doubt concerning the structure of the molecule, with the majority of investigators (12, 15, 20) favoring a trigonal bipyramid (D_{3h}) structure. The recent view by Abel (1) cites the accumulated evidence which seems to establish this structure firmly.

Since the investigation by King and Lippincott (12) there have been no revised computations of the thermodynamic functions of iron pentacarbonyl. In the present work the thermodynamic functions C_p° , S° ($H^\circ - H_8^\circ$), and $-(F^\circ - H_8^\circ)/T$ for iron pentacarbonyl have been computed at 298.15° K. and at 100° intervals to 1500° K., using the complete Raman spectrum reported by Stammreich and coworkers (20) and the infrared data of McDowell and Jones (15) and Bor (4) to revise the frequency assignments of King and Lippincott. However, the value of 753 cm^{-1} for ν_{16} which was reported by Stammreich and coworkers has not been used because of the uncertainty attending it, as described by McDowell and Jones.

As with nickel carbonyl, the rigid rotator harmonic oscillator approximation has been employed, and computations have been performed on a Burroughs 220 digital computer. A symmetry number of 6 is used, and the moments of inertia are those of Leadbetter and Spice (14). In Table III are presented the computed values of the thermodynamic functions.

In Table IV the results obtained at 298.15° K. are compared with the results of other investigators. The sensitivity of the computed values to the choice of frequency assignments is evident. Leadbetter and Spice (14) obtain best agreement with their calorimetric result by combining the assignments of Cotton and coworkers (5) with those of King and Lippincott (12), but the most recently published frequencies tend to result in lower values of the computed functions. The tetragonal pyramid model cannot be dismissed on the basis of these results.

The thermodynamic equilibrium constant for the reaction $\text{Fe}(s) + 5\text{CO}(g) = \text{Fe}(\text{CO})_5(g)$ has been determined in the same fashion as for nickel carbonyl. The heat of formation of $\text{Fe}(\text{CO})_5$ has been reported by Cotton, Fisher, and Wilkinson (6) as -182.6 ± 1.7 kcal./mole. Using this value, together with the heat of vaporization of 9.6 kcal./mole reported by Leadbetter and Spice (16) the entropy computed in the present work, and other data from

standard sources (8, 21), a value of -40.9 kcal./mole is obtained for the standard heat of reaction at 298.15° K., and a value of -137.6 is obtained for $\Delta S_{298.15}^\circ$. The equation for the equilibrium constant is then:

$$\log_{10}K_a = 8940/T - 30.09 \quad (6)$$

evaluated at 25° C. If the calorimetric entropy of Leadbetter and Spice is preferred, Equation 6 becomes:

$$\log_{10}K_a = 8940/T - 29.77 \quad (7)$$

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