The Heat Capacity of Nickel Carbonyl and the Thermodynamics of its Formation from Nickel and Carbon Monoxide.

By J. E. SPICE, L. A. K. STAVELEY, and G. A. HARROW.

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Values are given for the heat of fusion of nickel carbonyl, for its melting point, and for its heat capacity between 90° and 270° K. Some discussion follows on the thermodynamics of the reaction $Ni + 4CO \rightleftharpoons Ni(CO)_4(g)$.

FEW measurements of the thermal properties of nickel carbonyl seem to have been made, in spite of its industrial and scientific importance. Accordingly, calorimetric measurements have been made for nickel carbonyl in the liquid-oxygen range. From the results, the standard entropy of the compound has been estimated; combined with other available data, this quantity permits some discussion of the equilibrium constant and heat content change of the reaction $Ni + 4CO \rightleftharpoons Ni(CO)_4(g)$.

EXPERIMENTAL

The greater part of this work was done at Oxford, with the calorimeter and experimental method described by Staveley and Gupta (*Trans. Faraday Soc.*, 1949, **45**, 50).

The nickel carbonyl was prepared by Mayer and Wibaut's method (*Rec. Trav. chim.*, 1937, **56**, 356) and was purified by bulb-to-bulb distillation *in vacuo*, followed by vacuum-distillation at 0° with a low-temperature column. All three fractions had the same vapour pressure of 126·5 mm. at 0°, compared with Anderson's value of 133·7 mm. (*J.*, 1930, 1653) and Wallis and Beynon's value of 130 mm. (personal communication from the Mond Nickel Company). The high purity of this specimen was, however, shown by the small melting range and the absence of any marked pre-melting effect.

The calorimeter was designed for use with condensed gases and volatile liquids, and this meant that the nickel carbonyl had to be introduced by distillation from a detachable trap, the loss in weight of which gave the weight of carbonyl used. Unfortunately, some decomposition occurred during this process, as it always does when nickel carbonyl is distilled. The carbon monoxide formed was therefore removed from the vacuum-system by means of a Töpler pump and its volume measured, from which allowance was made for the nickel carbonyl lost by decomposition. The same procedure was followed when the nickel carbonyl was removed at the conclusion of the measurements, and a second figure for the weight used was thus obtained. This second figure (5·264 g.) was about 1% lower than the first (5·309 g.). Since decomposition of the nickel carbonyl during its removal from the calorimeter vessel was much more extensive than during its introduction (18% as against 3%) the first figure of 5·309 g. was considered the more reliable, and was used in the calculations. Throughout the measurements, the calorimeter vessel was filled with carbon monoxide (to a pressure of about half an atmosphere at room temperature) in order to prevent decomposition of nickel carbonyl vapour at the higher temperatures.

Measurements of the heat of fusion of nickel carbonyl were made subsequently at Liverpool, in order to provide some check on the reliability of the Oxford results. (It should be emphasised that any systematic error in these results is due to the uncertainty in the weight of nickel carbonyl in the calorimeter, and not to any other defect in the experimental method.) A different type of calorimeter was used (details will appear in a forthcoming paper) in which the weight of carbonyl in the calorimeter vessel was found without ambiguity by direct weighing. The calorimeter vessel was much larger than in the Oxford apparatus, holding about 50 c.c. of liquid as against about 5 c.c. In this later work, the nickel carbonyl was kindly supplied by the Mond Nickel Company; the only impurity was stated to be about 0·003% of iron pentacarbonyl, and the compound was therefore used without further purification.

RESULTS

Melting Point and Purity.—The following figures were obtained for the melting point of the nickel carbonyl, by using the Oxford calorimeter :

Percentage melted	30	48	65	83
Temperature (°K)	$253{\cdot}84_8$	$253{\cdot}84_9$	$253{\cdot}85_1$	$253{\cdot}85_2$

The usual extrapolation gives 253·86° K as the m. p. of the pure compound, and from the melting range, the liquid-soluble solid-insoluble impurity in the carbonyl is found to amount to 0·01 mole %.

The only value in the literature for the m. p. of nickel carbonyl is that of —25° (248° K) given by Mond (*J.*, 1890, **57**, 749). The present value, nearly 6° higher, is probably correct to ±0·05° K, the uncertainty being due to the temperature scale used in this work. Wallis (personal communication from the Mond Nickel Company) gives the m. p. as 254·0° K.

Heat Capacity.—Heat-capacity measurements extended from 90° K to the ice-point, and values taken from the smoothed curve are given in the Table at temperature intervals of 5°. The mean percentage deviation of the experimental heat-capacity values from the smoothed curve amounts to 0·65% over the whole range, and to 0·5% over the range from 125° K upwards. The possible error in the heat capacity of the empty calorimeter (which of course is used in deriving the molar heat capacity of the carbonyl) is taken into account in obtaining these values, so that the possible unsystematic error of the experimental heat capacities is as just stated.

Temp. (K)	C_p (cal./mole)	Temp. (K)	C_p (cal./mole)	Temp. (K)	C_p (cal./mole)	Temp. (K)	C_p (cal./mole)
90°	21·80	145°	29·95	200°	35·61	Fusion	
95	22·64	150	30·64	205	35·92	255°	48·03
100	23·43	155	31·30	210	36·21	260	48·09
105	24·19	160	31·91	215	36·49	265	48·15
110	24·92	165	32·51	220	36·74	270	48·23
115	25·61	170	33·00	225	37·00	275	48·32 †
120	26·32	175	33·50	230	37·25	280	48·42
125	27·03	180	33·95	235	37·46	285	48·54
130	27·77	185	34·39	240	37·66	290	48·67
135	28·50	190	34·80	245	37·82 *	295	48·80
140	29·25	195	35·21	250	37·93 *	300	48·94

* Corr. for pre-melting. † From this point onwards, values were determined by extrapolation of the smoothed curve, and are therefore subject to a greater uncertainty than the other values.

Heat of Fusion.—The following values were obtained with the Oxford calorimeter: 3305·6, 3308·1, 3303·3 cal./mole (mean, 3306 ± 2·5). The confirmatory measurements at Liverpool were made when the calorimetric technique used was relatively undeveloped; consequently, the results showed less agreement among themselves. Four values for the heat of fusion were obtained, with a mean value of 3295 ± 15 cal./mole. Having regard to this greater uncertainty, it is felt that these " Liverpool " results do confirm the " Oxford " values for the heat of fusion and hence for the heat capacity of nickel carbonyl. It should in any case be noted that the figure taken for the weight of nickel carbonyl in the Oxford calorimeter is an upper limit for this quantity. Had the calorimeter actually contained less carbonyl, a higher rather than a lower value would be indicated for the heat of fusion. Thus, we feel that the heat capacities quoted can be relied upon to ~±0·8%, and the heat of fusion to ~±0·25%.

Standard Entropy.—Although heat capacities have not been measured for temperatures below 90° K, it is of interest to estimate the standard entropy of nickel carbonyl. The method of extrapolation developed by Parks and his co-workers (Kelley, Parks, and Huffman, *J. Phys. Chem.*, 1929, **33**, 1802; Parks, Shomate, Kennedy, and Crawford, *J. Chem. Phys.*, 1937, **5**, 359) may be used. In this, the heat capacities at 90° and 120° K, derived from the experimental heat-capacity curve, are compared with the corresponding values taken from a " standard " curve extending down to liquid-hydrogen temperatures. The experimental curve is thus extrapolated to liquid-hydrogen temperatures, and a value for the entropy at 90° is derived. Parks *et al.* concluded that a considerable number of compounds could be grouped into two classes, each with its standard curve. The method has no adequate theoretical foundation, but in practice gives fairly reliable results provided that the molecules are not too different in size and shape from those of the " standard " substances. In the present case, the comparison has been made not only with Parks's " Class I " and " Class II " compounds but also, according to the same method, with 2 : 3 : 4-trimethylpentane, for which the heat capacities were measured by Pitzer and Scott (*J. Amer. Chem. Soc.*, 1941, **63**, 2419). The resulting values for the entropy at 90° K of solid nickel carbonyl are 18·31, 20·63, and 20·58 cal. °K^{-1} mole^{-1} respectively, when these three comparisons are made. As expected, there is some uncertainty, and in the absence of more precise information we take the entropy at 90° K of nickel carbonyl as 20·6 cal. °K^{-1} mole^{-1}. Needless to say, the use of an extrapolation procedure will introduce a large error into the final figure for the entropy, if the compound actually undergoes a solid transition within the extrapolation region. Nickel carbonyl is unlikely to do this since its entropy of fusion (13·0 cal. °K^{-1} mole^{-1}) is comparable with the entropies of fusion of solids of similar molecular shape and complexity, which also lack transitions.

Many different values have been reported for the heat of vaporisation of nickel carbonyl. Those derived from vapour-pressure data include 6500 (Dewar and Jones, *Proc. Roy. Soc.*, 1903, *A*, **71**, 427), 6700 (Wallis and Beynon, *loc. cit.*), 6920 (Anderson, *loc. cit.*), and 7200 cal./mole (Suginuma and Satozaki, *Bull. Inst. Phys. Chem. Res., Tokyo*, 1942, **21**, 432). The mean of two direct determinations by Wallis and Beynon (*loc. cit.*) gave 6300 cal./mole. We shall now assume a value of 6500 cal./mole at 298·16° K, since we attach greater weight to the value determined directly than to the values obtained from vapour-pressure measurements. Although this value is probably the best obtainable from the existing data, the entropy of vaporisation thus calculated (21·8 cal. °K^{-1} mole^{-1} at 298·16° K) is lower than would be expected from the Hildebrand–Trouton rule (Hildebrand, *J. Chem. Phys.*, 1939, **7**, 233). Thus, the entropy of vaporisation of carbon tetrachloride at the same molecular concentration of the saturated vapour is 22·2; yet nickel carbonyl is a less compact molecule than carbon tetrachloride, and so might be expected to have a greater entropy of vaporisation.

The standard entropy of nickel carbonyl is now computed as follows :

	cal. °K^{-1} mole^{-1}
S for solid at 90° K (Parks's extrapolation)	20·6
ΔS for solid, 90—253·86° K, graphical	31·5
$\Delta S_{\text{fusion}} = 3306/253{\cdot}86$	13·0
ΔS for liquid, 253·86—298·16° K, graphical	9·8
$\Delta S_{\text{vaporisation}} = 6500/298{\cdot}16$	21·8
Entropy for vapour at 298·16° K and 38·7 cm.*	96·7
ΔS for compression from 38·7 to 76 cm.	−1·3
S° for $Ni(CO)_4$ (298·16° K)	95·4

* Wallis and Beynon, *loc. cit.*

(Because of the manifest uncertainties in the above calculation, it is not worth while to apply the correction for gas imperfections.)

Crawford and Cross (*J. Chem. Phys.*, 1938, **6**, 525) calculated the thermodynamic functions of nickel carbonyl from their assignment of the vibration frequencies of this molecule, and they obtain S° (at 298·16° K) = 97·0. In view of the approximate nature of the present calculation, the agreement between calorimetric and spectroscopic entropies is as close as could be expected.

The Thermodynamics of the Formation of Nickel Carbonyl from Nickel and Carbon Monoxide.

Equilibrium Measurements.—Mittasch (*Z. physikal. Chem.*, 1902, **40**, 1) carried out an exhaustive study of the equilibrium $\mathrm{Ni} + 4\mathrm{CO(g)} \rightleftharpoons \mathrm{Ni(CO)_4(g)}$ and we shall now consider his results together with information on the heat content and entropy changes for this reaction. Mittasch used a static method, and his equilibrium constants, although self-consistent and reproducible for a given filling of his apparatus, varied markedly from one filling to another, and in particular were greatly influenced by the physical form of the metallic nickel present in the vessel.

Mittasch (*loc. cit.*, pp. 21 and 23) gives an expression for $K = [\mathrm{CO}]^4/[\mathrm{Ni(CO)_4}]$, the equilibrium constant of the decomposition reaction, which is actually neither K_c nor K_p. Moreover, the values of K given later in the paper are in fact calculated from the expression $(p - P)^4/[27(4P - p)(1 + \alpha\theta)^3]$, and not from the corresponding expression involving $(p - P)$ rather than $(p - P)^4$ which appears in error on pp. 21 and 23 of the paper. In Mittasch's notation, P (sometimes P_θ) is the pressure in mm. which would have been exerted by the nickel carbonyl vapour at $\theta°$ C, if no decomposition had occurred; p (or p_0) is the actual pressure in mm. at $\theta°$ C; α is the temperature coefficient of the pressure of a perfect gas. The correct expression for the equilibrium constant of the formation reaction is:

$$K_p = p_{\mathrm{Ni(CO)_4}}/p_{\mathrm{CO}}^4 = \frac{(4P - p) \times 27 \times 760^3}{(p - P)^4 \times 256}$$

The relation between this K_p and Mittasch's K is:

$$\log_{10} K_p = -\log_{10} K + 6{\cdot}234 - 3\log_{10}(1 + \alpha\theta)$$

Mittasch gives three main series of equilibrium results—series 2, 5, and 6 on pp. 46—47 of his paper—and for each series $\log_{10}K_p$, when recalculated as above, gives a good linear plot against $1/T$. The interpolated values of $\log_{10} K_p$ at 298° K, together with the corresponding $\Delta H°$ and $\Delta G°$ values for the reaction, are then as follows:

	$\log_{10} K_p$ at 298° K	$\Delta G°$ (kcal.)	$\Delta H°$ (kcal.)
Series 2	1·67	−2·3	−26
Series 5	2·62	−3·6	−27·5
Series 6	3·32	−4·5	−30

Heat of Reaction.—Reicher (" Werken von het Genootschap ter bevordering der natuur-, genees- en heelkunde," Amsterdam, 1896, 2nd Series, Vol. II, p. 296) found the heat of combustion of liquid nickel carbonyl at constant volume to be 270·8 kcal./mole. Combining this with the aforementioned figure of 6·5 kcal./mole for the heat of vaporisation, and with accepted values for the other necessary heats of formation (" Selected Values of Chemical Thermodynamic Properties," Nat. Bur. Standards, Circular 500), we obtain for the reaction $\mathrm{Ni} + 4\mathrm{CO\ (g)} \rightleftharpoons \mathrm{Ni(CO)_4\ (g)}$, $\Delta H° = -52{\cdot}6$ kcal. Mittasch (*loc. cit.*, p. 48), using a direct method, found the heat of formation of liquid nickel carbonyl from nickel and carbon monoxide at constant pressure to be 52·17 kcal./mole. From this, the value for gaseous nickel carbonyl is $\Delta H° = -45{\cdot}67$ kcal. Finally, experiments carried out in the Clydach laboratory of the Mond Nickel Company (personal communication from the Company) gave values of −34·5 kcal. (direct method) and −36·3 kcal. (indirect method). The values are summarised as follows:

$\Delta H°$ (*kcal.*) *for the reaction* $\mathrm{Ni} + 4\mathrm{CO\ (g)} \rightleftharpoons \mathrm{Ni(CO)_4\ (g)}$.

From heat of combustion (Reicher)	−52·6
Direct determination (Mittasch)	−45·7
From d $(\log_{10} K_p)/\mathrm{d}T$ (Mittasch): Series 2	−26·0
Series 5	−27·5
Series 6	−30·0
Direct determination (Mond Nickel Co., 1936)	−34·5
Indirect determination (Mond Nickel Co., 1950)	−36·3

The discrepancies are somewhat startling. Reicher gives little information about his experimental method, but Mittasch's direct determinations were apparently well-planned and carefully executed. One would not expect the values from the temperature coefficient of the equilibrium constant to be as reliable as the results of direct determinations (especially in view of the uncertainty attaching to Mittasch's equilibrium constants), so we accept the two modern determinations made by the Mond Nickel Company as likely to be the most accurate. Accordingly, we take a mean value of $\Delta H^{\circ} = -35$ kcal. This gives, for the formation of nickel carbonyl from its elements, $\Delta H_f^{\circ} = -140{\cdot}6$ kcal./mole for the gaseous compound, and $\Delta H_f^{\circ} = -147{\cdot}1$ kcal./mole for the liquid.

ΔS° *and* ΔG° *for the Reaction.*—We use the following values for standard entropies (at 298·16° K) :

Nickel carbonyl	97·0	(Crawford and Cross, *loc. cit.*)
Nickel	7·14	(Busey and Giauque, *J. Amer. Chem. Soc.*, 1952, **74**, 3157)
Carbon monoxide	47·30	(Clayton and Giauque, *ibid.*, 1932, **54**, 2610)

Then for the formation of gaseous nickel carbonyl from nickel and carbon monoxide, we have $\Delta S^{\circ} = -99{\cdot}3$ cal. °K^{-1} mole^{-1} (at 298·16° K). Combining this with the above value for ΔH°, we have $\Delta G^{\circ} = -5{\cdot}4$ kcal., and $\log_{10} K_p = 3{\cdot}96$ (at 298·16° K) for the reaction $\mathrm{Ni} + 4\mathrm{CO} \rightleftharpoons \mathrm{Ni(CO)_4(g)}$. These values seem in fairly satisfactory agreement with those derived from Mittasch's equilibrium measurements ($\Delta G^{\circ} = -2{\cdot}3$ to -4.5 kcal.; $\log_{10} K_p = 1{\cdot}67$—$3{\cdot}32$) in view of the uncertainties inherent in the whole question.

The scatter of Mittasch's results is undoubtedly due to variations in the chemical potential of the solid nickel in equilibrium with gaseous nickel carbonyl and carbon monoxide. Giauque (*J. Amer. Chem. Soc.*, 1949, **71**, 3192) has recently shown that the true equilibrium corresponding to a solid, macrocrystalline phase in contact with gases, may be impossible of attachment when the solid is present in a finely divided form. Thus, the heat content of finely divided magnesium oxide, made by dehydrating the hydroxide *in vacuo* at a fairly low temperature, was greater by 888 cal./mole than that of crystalline magnesium oxide, while the free energy was greater by 800 cal./mole. Giauque attributes this difference to the possession by the finely divided sample of a more open structure, of higher energy content, than that of the macrocrystalline phase. The same thing may well be true of the metallic nickel present in the nickel carbonyl equilibrium, although the numerical data are not sufficiently precise to permit even a semiquantitative discussion in these terms. The experimental realisation of the equilibrium under discussion must necessarily involve finely divided nickel, so that it may be that significant equilibrium constants cannot possibly be obtained by direct measurements. Moreover, a direct determination of ΔH° must similarly involve finely divided nickel, and a significant value for this quantity may have to be derived from accurate determinations of the heat of combustion of nickel carbonyl.

Since the completion of the main part of this paper, we have seen a preliminary report of direct measurements of the nickel–nickel carbonyl equilibrium over the temperature range 49—94° C (Tomlinson, Abst. Papers presented at the 125th Mtg. Amer. Chem. Soc., March 1954, p. 180). The results are summarised in the equation ΔG° (cal.) $= -31{,}972 + 87{\cdot}92T$ (°K), for the reaction $\mathrm{Ni} + 4\mathrm{CO} \rightleftharpoons \mathrm{Ni(CO)_4(g)}$, whence ΔG° (at 298·16° K) $= -5{\cdot}8$ kcal., in good agreement with our value of $-5{\cdot}4$ kcal., derived from the heat content and entropy changes for the reaction. The above equation, however, also gives $\Delta H^{\circ} = -32{\cdot}0$ kcal. and ΔS° (at 298·16° K) $= -87{\cdot}9$ cal. °K^{-1} mole^{-1}, and Tomlinson claims that the latter figure indicates that Crawford and Cross's value of 97·0 for the standard entropy of nickel carbonyl is about 11 cal. °K^{-1} mole^{-1} (or 10%) too low. We would merely point out (*a*) that our calorimetric measurements confirm Crawford and Cross's value, and could not possibly give a value as high as 108 cal. °K^{-1} mole^{-1} for the standard entropy of nickel carbonyl, and (*b*) that Tomlinson's values for ΔH° and ΔS° are based on the temperature coefficient of ΔG°, and are therefore subject to greater uncertainty than ΔG° itself.

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INORGANIC CHEMISTRY LABORATORY, SOUTH PARKS ROAD, OXFORD.
DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY,
UNIVERSITY OF LIVERPOOL.

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